Solubility Studies and Growth of 4-aminobenzophenone Single Crystal: a Potential Organic NLO Material

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Abstract The solubility and growth aspects of 4-aminobenzophenone (4-ABP) was investigated with an intention to grow bulk and good quality crystal. The solubility of 4-ABP in various organic solvents such as ethyl acetate, ethanol and O-xylene were studied. From the investigation, it was realized that the 4-ABP material has highest solubility in ethyl acetate whereas it has the lowest solubility in pure O-xylene solvent. Single crystals of 4-ABP were grown by solution growth using ethanol as a growth medium which has the moderate solubility when compared to other solvents. The structural and optical properties of the grown 4-ABP samples were studied. The lattice parameters of the 4-ABP were calculated using X-ray diffraction analysis which confirmed the monoclinic structure of the grown material. The optical transmission study showed that the 4-ABP has about 70% of transparency in the visible and near infrared region

1. INTRODUCTION

Organic materials are promising for nonlinear optical (NLO) applications because of their high NLO efficiency and fast response than their inorganic counter parts. Benzophenone and its derivatives are potential organic NLO material with good optical, mechanical properties, and non hygroscopic nature [1, 2]. Moreover, the derivatives of benzophenone are attracted by many researchers due to their large NLO susceptibilities and short cut-off wavelengths up to deep UV region (< 400 nm) [3]. Among the benzophenone derivatives, 4-amino benzophenone (4-ABP) is the most significant one with the second harmonic generation (SHG) efficiency of 360 times that of Ammonium dihydrogen Phosphate (ADP) [3, 4]. The 4-ABP crystal belongs to the monoclinic crystal system with space group P21 and cell parameters a = 12.036 Å, b = 5.450 Å, c = 8.299 Å, and β = 97.841°. Even though several reports are available on the growth aspect of 4-ABP, growth of high quality, inclusion free bulk crystal of 4-ABP is still remaining as a difficult task due to its growth related issues. Moreover, it is difficult to grow 4-ABP single crystal from solution, because it is readily photo-oxidized [5] in solution which results pink colored impurity and it can be easily incorporated into growth sectors of the transparent crystal [5]. For the growth of 4-ABP, several organic solvents such as ethanol, methanol, dimethyl formamide (DMF) were used as the growth medium in the literature [5, 6]. Pan et al. [6] investigated the effect of ethanol, methanol and DMF solvents on the growth of 4-ABP crystals. Recently, the 4-ABP single crystal with dimensions of $30 \times 9 \times 6 \text{ mm}^3$ was grown by using ethyl acetate as a solvent by Natarajan et al [7]. However, lots of inclusions were found in the grown crystals from ethyl acetate solution which resulted low quality crystals with less transparency.

In this present investigation, the solubility of 4-ABP was measured in three different solvent at ambient temperature and relatively inclusion free 4-ABP crystal was grown by using ethanol as a growth medium. The XRD and optical transmission studies were carried out on the grown crystals to analyze the structural and optical properties of the 4-ABP.

2. SOLUBILITY AND CRYSTAL GROWTH OF 4-ABP.

The commercially purchased 4-ABP material was purified by recrystallization process using ethanol. In the solution growth process, the solvent can influence the morphology of the crystal due to its interaction with the surfaces of the growing crystal. Therefore, the selection of suitable solvent for crystal growth is more important in solution growth. The solubility of the 4-ABP in various organic solvents viz., the ethyl acetate, the ethanol, and o-xylene was measured at ambient temperature. From the investigation, it was found that the 4-ABP material has highest solubility in ethyl acetate (17 g/100 ml) whereas it has the lowest solubility in pure O-xylene (1 g/100 ml). But, it has moderate solubility in ethanol (10 g/100 ml). In general, if the solubility is too high, it is difficult to grow good quality large size crystal as it is difficult to control the number of nucleation. On the other hand, too low solubility is also not suitable to grow crystal with reasonable size due to low availability of solute molecules. Therefore, ethanol was chosen as a growth medium for the present work and the saturated solutions of 4-ABP was prepared by dissolving the refined source material into ethanol. The prepared saturated solutions were homogenized by continuous mild stirring of the solutions using a magnetic stirrer by maintain the temperature of the solution. Then, the near saturated solutions were transferred into a crystallizer and covered by a perforated polyethylene sheet for controlled evaporation at room temperature. After the growth period of 7 days, we obtained the relatively inclusion free and platelet crystals from the growth solution prepared by using ethanol. The photograph of the harvested crystal from ethanol is shown in Fig.1.



Figure 1: Photograph of the 4-ABP crystal grown from ethanol.

3. RESULTS AND DISCUSSION

At the initial stage the growth solution was looked as pale yellow color and when the time increases, the solution turned to dark yellow in color. This color variation is possibly due to photo oxidation of the growth solution [6]. Moreover, the grown crystal also looks like dark yellow in color. However, the crystal is relatively inclusion free as can be seen in the Fig.1, when compared to our previous crystal grown in ethyl acetate solution [7]. Low growth rate of the crystal (compared to crystal grown from ethyl acetate) is the possible reason for the low solvent inclusion. Further investigation is going on to improve the quality of the crystal by mixed solvent approach and the outcome will be published elsewhere. The structural properties of the grown crystals were studied by X-ray diffraction (XRD) analysis using Rigaku X-ray diffractometer. Optical transmission study was performed at UV Vis-NIR region to determine the range of transmission/absorption of the grown crystals.

3.1 X-ray diffraction analysis of the grown samples

The recorded X-ray diffraction spectrum for the fine powdered 4-ABP sample is shown in Fig. 2. The sharp and strong diffraction peaks of the grown samples illustrate the crystalline quality of the samples. The diffraction peaks of the XRD spectra were indexed and thus lattice parameters of the crystal were calculated using the crystallographic equation. The 4-ABP crystal belongs to monoclinic crystal system with P21 space group. The calculated lattice parameters of 4-ABP sample are a = 12.35 Å, b = 5.59 Å, c = 8.487 Å and β = 97.41° and the calculated parameters were well agreed with the reported values [4].



Figure 2: X-ray diffraction spectrum for the fine powdered 4-ABP.

3.2 optical transmission studies

Figure 3 shows the optical transmission spectrum of 4-ABP crystal. The polished crystal used for the optical studies had the thickness of about 1 mm. The dark yellow colored 4-ABP crystal grown from the ethanol medium shows the transparency of about 70% in the visible and NIR region. The cut off wavelength of 4-ABP was observed at about 400 nm. From the result, it is obvious that the 4-ABP sample is suitable for green laser generation.



4. CONCLUSION

Single crystals of 4-ABP were grown by solution growth using ethanol as a growth medium. The grown crystals were relatively inclusion free when compared to crystals grown from other solvents. The growth aspects of the crystals were analysed based on solute-solvent interactions. The structural and optical properties of the samples were investigated. It was confirmed that the 4-ABP was crystallized with monoclinic crystal system from the X-ray diffraction analysis. The 4-ABP crystal had relatively better transparency in the visible region with cut off wavelength of 400 nm.

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Comparison of Mechanical Performance of Hybrid Vinybased Composites reinforced with Coir/Sisal and Sisal/Kenaf Fibres

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The effect of diameter, test length and test speed on the tensile

Abstract: Considerable research in the field of material science has been directed towards the development of new light weight, high performance engineering materials like composite. In many applications, like an aircraft, there is a need for high strength weight ratio. This can be achieved by composite consisting of low density (and soft) matrix reinforced with stiff fibres. Now a day's attention has been focused in the development of natural fibre composite due to their low cost and easy renewability. In this investigation the mechanical properties of Hybrid fibre reinforced vinyl ester composites were analysed based on volume percentage and length of fibre ,similarly single natural fibre composite were developed to compare the properties. The tensile and impact strength increase with fibre length and fibre content ,on the other hand flexural strength decrease with fibre length and content.

Keywords: Hybrid fibre composites; Vinyl ester; Mechanical properties; Regression models.

1. INTRODUCTION

In recent years, utilization of composite material in many engineering fields has undergone a tremendous increase. The background of the research that has been carried out is the awareness that the demand of coir, sisal and kenaf products is slowly decreasing and that other profitable markets have to be found for this commodity. The best way to bring the existing coir-sisal, kenaf industry to a higher level is the development of new coir sisal and kenaf products with higher added value of mechanical properties. One possible technology that could fulfil this goal is the use of coir-sisal fibre in composite components .Coir is a versatile lignocellulosic fibre obtained from coconut trees (Cocos nucifera), which grow extensively in tropical countries. Because of its hard wearing quality, durability and other advantages, it is used for making a wide variety of floor-furnishing materials, yarn, rope, etc. [1]. However, these traditional coir products consume only a small percentage of the total world production of coconut husk. Coir is a cheap fibre, even cheaper than sisal and jute [2]. Coir fibres are not as brittle as glass fibres, are amenable to chemical modification, are non-toxic and possess no waste disposal problems, but unfortunately the performance of coir as a reinforcement in polymer composites is unsatisfactory and not comparable even with other natural fibres. This inferior performance of coir is due to various factors such as its low cellulose content, high lignin content, high microfibrillar angle, and large as well as variable diameter. Sisal fibre is hard fibre extracted from the leaves of the sisal plant (Agave sisalana). Though native to tropical and subtropical North and South America, sisal plant is now widely grown in tropical countries of Africa, the West Indies and the Far East [3].

strength, initial modulus and percent elongation at the break of sisal fibre is studied. They concluded that no significant variation of mechanical properties with change in fibre diameter was observed. However, the tensile strength and percent elongation at the break decrease while Young's modulus, increases with fibre length [4]. The optimum fibre parameters and their influence on the mechanical properties for coir-polyester resin were studied and the results are shown that the fibre content in weight percentage is playing major role than the fibre length on the improvement of tensile, flexural, and impact strength properties [5].Beside a number of investigations have been conducted on the natural fibre hybrid composite to study the effect of hybridisation of these fibre on the mechanical properties. The tensile strength of plain weave hybrid ramie-cotton fabrics polyester matrix composite was determined as a function of volume fraction and orientation of ramie fibre [6]. The dynamic properties such as storage modulus, damping behaviour and static mechanical properties such as tensile, flexural and impact of randomly oriented intimately mixed short banana/sisal hybrid fibre reinforced polyester composites a function of total investigated[7]. The effect of concentration and modification of fibre surface in sisal/oil palm hybrid fibre reinforced rubber composites have been studied [8].Water absorption behaviour, the effect of temperature of immersion ,fibre volume fraction and three drying of fabrics before there incorporation and to the composite of sisal/cotton, jute/cotton and ramie/cotton hybrid fabric reinforced composite were evaluated [9].Statics and dynamics mechanical properties kenaf fibres and wood floor hybrid polypropylene composites were studied [10]. The optimum fibre parameters and their influence on the mechanical properties for coir-polyester resin were studied and the results are shown that the fibre content in weight percentage is playing major role than the fibre length on the improvement of tensile, flexural, and impact strength properties. Since most data in literature cover only a specific loading fraction of fibres, this work was aimed at analyzing

the mechanical behaviour of hybrid fibre vinyl ester composites covering short fibre length and volume fractions.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

2.1.1 Coir

Coir is lignocellulosic natural fibre. Its seed hair fibre obtained from outer shell, or husk of coconut, fruit of the cocus nusifera. The coarse, stiff, reddish, brown fibre made of small thread, each of about 0.03 to 0.1cm long and 12 to $24\mu m$ in diameter composed of lignin, woody plant substance, and cellulose. The individual fibre are narrow, with thick walls made of cellulose. They are pale when immature but later hardened become yellowed as a layer of lignin on their walls.

2.1.2 Sisal

Sisal is another natural fibre obtained from the leaves of a plant. It is most produced natural fibre after cotton. Sisal, also known as sisal hemp is a plant that yields a stiff fibre and is mostly used for making rope. The fibre is smooth and straight and light yellow in colour. It is fairly coarse and it is extensively used because of its strength, durability, ability to stretch, affinity for certain dyestuffs, and resistance to deterioration in saltwater.

2.1.3 Kenaf fibre

Kenaf is one of the allied fibres of jute and shows similar characteristics. Other names include Bimli, AmbaryAmbari Hemp, Deccan Hemp, and Bimlipatum Jute. It is an annual or biennial herbaceouplant (rarely Short-lived perennial) growing to 1.5-3.5 m tall with a woody base. The stems are 1–2 cm diameter.

2.1.4 Vinyl ester resin

It's one of the Addition polymers. It acts as a good binder for fibre, excellent physical properties including good toughness and good impact properties. Curing time is also less compare to other resin. Vinyl ester combines inherent toughness with outstanding heat and chemical resistance, Corrosionresistance, and Possesses low ester content and low instauration resulting in greater resistance to hydrolysis and less shrinkage during cure. The Properties of vinyl ester is shown in Table 2.

The untreated natural fibre were cut for the dimensions of 10, 20, and 30 mm length and fibre content in volume percentage of 20, 30, and 40, respectively. The two parameters and three levels contributed total of nine combinations, and these combinations were planned using Design of Experiments. The simple hand lay-up process was followed for fabricating Hybrid–vinyl ester composites. The Properties of coir, sisal and kenaf is shown in Table 1

| Properties | Coir | Sisal | Kenaf |
|--|----------|---|---|
| Cellulose (wt%) | 36-43 | 67-78 | 75-90 |
| Young's modulus (Gpa) | 4-6 | 55-12.6 | 35-40 |
| Tensile strength (MPa) | 131-175 | 468-640 | 350-600 |
| Lignin (wt%) | 0.5-0.25 | 8-11 | 7-8 |
| Density(gm/cm) | 1.25 | 1.33 | 1.5 |
| Property | | Vinyl-e Dark vel | ster resin low colour |
| Property Appearance | | Vinyl-e Dark yel | ster resin inv. colone |
| Property Appearance Viscosity(cps) | | Vioyt-e Dark yel | ster resin Inw colone 00 |
| Property Appearance Viscosity(cps) Density(gro/ce) | | Vioyl-e Dark yel 7 | ster ræsin Inve colonæ 00 19 |
| Property Appearance Viscosity(cps) Density(gro/cc) Elorgation at break (%) | | Viayl-e Dark yel 7 1 | ster resin inw colone 00 19 3 |
| Property Appearance Uncenity(eps) Density(gro/cc) Elorgation at Irreak (%) Teasile strengti(Mpa) | | Vinyl-e Dark yel 7 1 | ster resin nw colour 00 19 3 10 |
| Property Appearance Viscosity(cps) Density(gm/cc) Elongation at lineak (%) Teasile strength(Mpa) Yorng's modulus(Mpa) | | Vinyl-e Dark yell 7 1 9 | ster resin anv colone 00 19 3 3 50 80 |
| Property Appearance Visconity(cps) Density(gro'cc) Elongation at lireak (%) Teasile strength(Mpa) Yoring's modulins(Mpa) Flexural strength(Mpa) | | Vinyl-e Dark yel 7 1 9 9 | ster resin anv. colone 00 19 3 3 00 80 80 80 |

Poly vinyl acetate release agent was applied to the surfaces before the mould. The fibres are proportionally mixed and were pre-impregnated with the matrix material consisting of unsaturated vinyl ester resin, promoter, cobalt octoate, accelerator, and MEKP catalyst. The impregnated layers were placed in the resin matrix (18×16 cm) and pressed heavily for 1 h before removal. After 1 h, the composites were removed from the mould and cured at room temperature for 24 h. The same procedure was followed to prepare different types of composites as per the nine combinations of fibre parameters. The fabricated hybrid composite is shown in Figure1.



Figure1. Fabricated fibre composite.

3. MECHANICAL TEST

3.1Tensile test

The tensile test is generally performed on flat specimens. The commonly used specimen for tensile test is the dog-bone specimen with end tabs. Test conducted by Tensometer testing machine (force range-up to 20KN,cross head travel-525mm excluding grip ,testing length-135mm between the grip, dc servometer-1,1Nm, controller-digital load and extension microprocessor)and cross-head speed of 5 mm/min as per ASTM D638-08. The tensile test specimen before and after testing is shown in Figure 2. The length, width, and thickness of each sample were approximately 165, 25, and 3 mm, respectively and results are analyzed to calculate the tensile strength of composites samples.



Figure 2. Tensile Specimen before and after testing.

3.2 Flexural strength

The flexural strength of a composite is the maximum tensile stress that it can withstand during bending before reaching the breaking point. The rectangular test pieces of $12.7 \times 12.7 \times 3$ mm dimension for flexural test were cut from the prepared Hybrid composite. Flexural test was conducted as per ASTMD790-07. The flexural test specimen while and after testing is shown in Figure 3. The three point bend test is conducted on all the composite samples in the universal testing machine Instron1195, cross head speed of 10 mm/min are maintained.



Figure 3. Flexural specimen while and after testing.

3.3 Impact strength

The impact strength of the samples was measured using ATS FAAR Impact tester (model No. 16.1 and capacity of up to 25 J) as per ASTMD256-06 standards. The test specimen was supported as a vertical cantilever beam and broken by a single swing of a pendulum. The pendulum strikes the face of the sample and total of five samples were tested and the mean value of the absorbed energy was taken. The impact test specimen before and after testing is shown in Figure 4.



Figure 4. Impact specimen before and after testing.

4. RESULTS AND DISCUSSION

4.1 Effect of length and fibre content in coir composite

Importance of mechanical analysis as a main tool in study of performance of natural fibre polymer composite is a paramount of importance. Mechanical properties of fibre reinforced composite depend on polymeric matrix, distribution and orientation of reinforcing fibre, nature of fibre-matrix interface and interface region. The coir vinylester composite exhibited maximum tensile strength Of 17.40MPa for the fibre length of 30 mm and fibre volume

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content of 40%. The increase of fibre length value and fibre content increase the tensile properties .The fibre length of 30mm and fibre volume content 20% vol exhibited maximum flexural strength of 38.5MPa. Increase the fibre content flexural strength start decreasing and impact behaviour of 162.84J/m for the fibre length of 30 mm and fibre content of 40%. Increase the fibre length and fibre content increase impact properties. The effect of length and fibre content in coir composite is shown in Figure 5



Figure 5. Effect of length and fibre content on coir composite.4.2 Effect of length and fibre content in coir/sisal composite

The coir/sisal vinyl-ester composite exhibited maximum tensile strength 0f 20.1MPa for the fibre length of 30 mm and fibre volume content of 40%. The increase of fibre length value and fibre content increase the tensile properties. The fibre length of 30mm and fibre volume content 20% vol exhibited maximum flexural strength of 39.4MPa.increase the fibre content flexural strength start decreasing and impact behaviour of 170 J/m for the fibre length of 30 mm and fibre content increase impact properties. The effect of length and fibre content increase impact properties. The effect of length and fibre content in coir/sisal composite is shown in Figure 6.



Figure 6. Effect of length and fibre content in coir/sisal composite.

4.3 Effect of length and fibre content in sisal/kenaf composite

The sisal/kenaf vinyl-ester composite exhibited maximum tensile strength of 22.1MPa for the fibre length of 30 mm and fibre volume content of 40%. The increase of fibre length value and fibre content increase the tensile properties .The fibre length of 30mm and fibre volume content 20% vol exhibited maximum flexural strength of 43.4MPa.increase the fibre content flexural strength start decreasing and impact behaviour of 172.84J/m for the fibre length of 30 mm and fibre content of 40%.increase the fibre length and fibre content increase impact strength. The effect of length and fibre content in sisal/kenaf composite is shown in Figure 7.



Figure 7 Effect of length and fibre content in sisal/kenaf composite

5. CONCLUSIONS

The investigation originally aimed at improvement of mechanical properties of natural fibre and replacement of glass fibre. The investigation reported that increase the fibre length and fibre content increase the tensile and impact properties but lowered the flexural strength. High tensile strength, flexural strength and impact strength reinforced with sisal/kenaf composite compared with coir and coir/sisal reinforcement. Hybridisation improve over all mechanical properties. The result hybrid vinyl ester composite with correct or optimum weight and correct length of fibres give the expected performance.

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Synthesis & Structural Study on Graphene Nano Particles

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Abstract: Graphene is one atom thick planar sheet of carbon atoms densely packed in a honey comb structure is the first stable twodimensional crystal lattice in nature, has grabbed appreciable attention due to its exceptional electronic, mechanical, electrical, optical, thermal and opt-electronic properties. Advancement of research in graphene, in the area of synthesis, properties and applications due to its wide range of applications in gas sensor, touch screen, magnetic, catalyst and electronic devices. In this present paper, we report on the synthesis of, Graphene Oxide, Graphene by a simple hydrothermal chemical co-precipitation (modified Hummers) method. Graphene oxide was effectively prepared by above process possesses different types of oxygen functionalities which allows GO to interact with organic and inorganic materials in covalent, non covalent or ionic manner. The GO was reduced by hydrazine hydrate as reducing agents to obtain graphene as end product. The prepared samples were characterized by X-ray diffraction (XRD), Raman, FT-IR, UV, Scanning Electron Microscopy (SEM) were reported.

Key Words: Graphene Oxide, Graphene, Raman, FTIR and SEM.

1. INTRODUCTION

Graphene consists of a single atomic layer of sp² hybridized carbon atoms that result in a hexagonal lattice. It is the basic building block for all sp² graphitic materials including fullerenes, carbon nano tubes, and graphite [1] has revolutionized the scientific frontiers in nano science, engineering technology and condensed matter physics due to its intrinsic and extrinsic physical and chemical properties [2]. Graphene and Graphene Oxide layers have been actively investigated and synthesized to build new novel materials. Around each carbon atom, three strong σ bonds are established with the other three surrounding carbon atoms, according to tight-binding, the valence and conduction bands touch at the Brillouin zone thus making graphene a zero band gap semiconductor [3]. Graphene, exhibits exceptional electronic, optical, magnetic, thermal and mechanical properties, including high values of its Young's modulus(1100GPa)[4], fracture strength (125GPa), [4] thermal conductivity (5000Wm⁻¹K⁻¹)[5], mobility of charge carriers (200000 cm² V⁻¹ s⁻¹),[6] specific surface area (calculated value, 2630 m²g⁻¹), [7] high chemical stability and high optical transmittance, quantum Hall effect at room temperature[8-10] and a tunable band gap. These novel materials have great potential applications such as electrochemical, energy storage, cell imaging, drug delivers and biosensors.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Graphene Oxide

Graphene Oxide was prepared from natural graphite powder by the modified Hummer's method [11]. 2g of Graphite powder and 1g of NaNO3 were taken in a 1L flask kept at 0°C and 46ml of Conc. H_2SO_4 was poured slowly under continuous stirring. Then 6g of KMnO₄ was slowly added and temperature of the mixture was maintained at 25°C. Then the solution is stirred for 2h, after that 92 ml of water was slowly dripped into the solution and stirred at 35°C for another 1hr. Adding 280 ml of water causes an increase in temperature to 100°C. Then, it was further treated with H_2O_2 (30%, 5 ml) after which the color of suspension changes to greenish yellow. The solution is washed 5 to 7 times with 5% warm solution of HCl and 250 ml of deionised water. The solution is filtered several times to get a fine black paste. Finally, the black paste is dried in oven for 24hrs at 80°C. Pure fine nano particles of black powder are obtained as Graphene Oxide.

2.2. Synthesis of Graphene

For the synthesis of Graphene, 1:5 ratios of hydrazine hydrate and deionised water solution is added slowly drop by drop to 1:1 ratio of Graphene Oxide and deionised water solution and the reaction is kept at 100°C for 3 hours under continuous magnetic stirrer and after that the solution is thoroughly washed with water and filtered. A dark black paste is collected and then the mixture is dried in oven for 24hrs at 80°C, a fine pure black soft and smooth powder particles are obtained as Graphene.

3. RESULT AND DISCUSSION

3.1. XRD analysis

The XRD studies were carried out for the Graphene Oxide which shows a major peak at 12.9° for corresponding (002) plane shown in fig.1 (b) with a "d" spacing of 6.87Å with the particle size of 13nm[12]. For Graphene, the predominant peaks are observed at 26.6° for (002) and 43° for (100) planes are shown in fig.1 (d) with an average particle size of 8.3 nm[4] for a "d" spacing of 3.34Å and 2.10Å. When Graphene Oxide is annealed at different temperatures, an intermediate stage of Graphene and Graphene Oxide known as reduced Graphene Oxide is also shown in fig.1(c) which has a peak value of 24.6° for (002) and 43.6° for (100) with a "d" spacing of 3.60Å and 2.07Å for an average particles size of 10.5 nm [13]. The pristine graphite crystal shows major peaks at 26.46° for (002) with "d" spacing of 3.36Å and other peaks are also illustrated in fig.1.(a)

having an average particles size of 18.9 nm. The particle size, dislocation density and strain constraints of the synthesized materials are calculated from XRD analysis for graphite, graphene oxide, reduced graphene oxide and graphene are given in table. 1

| Table 1. Calculations of Particle size, Dislocation Density |
|---|
| and Micro strain for graphite, graphene oxide, reduced |
| graphene oxide and graphene |

| Mater- ials | 20 | FWH M | Particle Size(nm) | Dis- location density 10 ¹⁵ lines m ⁻ 2 | Micro strain 10 ⁻³ line ⁻ ² m ⁻⁴ |
|----------------|------|----------|----------------------|--|--|
| GO | 12.9 | 0.6 | 13.0 | 5.62 | 2.60 |
| | 24.6 | 0.6 | 13.0 | 0.14 | 4.24 |
| RGO | 43.6 | 1 | 8.5 | 0.13 | 4.04 |
| | 26.6 | 1 | 8.1 | 0.14 | 4.24 |
| G | 43 | 1 | 8.5 | 0.13 | 4.05 |
| GR | 26.4 | 0.34 | 23.0 | 1.81 | 1.44 |



Figure. 1 The XRD patterns of (a) Graphite, (b) Graphene Oxide, (c) Reduced Graphene Oxide and (d) Graphene

3.2 RAMAN SPECTROSCOPY

The Raman spectrum of the pristine graphite, as expected, displays a prominent G peak at 1577 cm⁻¹ corresponding to the first order scattering of the E_{2g} mode and D peak at 1351cm⁻¹ due to the presence of minimum number of sp² hybridization atoms stacking in basal plane of sub lattice crystalline in nature. In addition to the G and D bands, another peak appears at 2701 cm⁻¹ is called 2D band. It arises due to the pure existing nature of sp² hybrid orbital stacked well in single layer structure of lattice arrangement depending upon the overlap of neighbouring atoms.

Graphene Oxide contains a G peak is the result of plane optical vibrations is due to first order resonance. It is also found that G band is broadened and shifted to 1572 cm^{-1} [60]. In addition, the D band is observed at 1336 cm⁻¹ becomes prominent, is indicating the reduction in size of the plane sp² domains, possibly due to the extensive oxidation [14]. Similarly, we observe the major peaks of G and D bands for the graphene at 1336 cm⁻¹ and 1572 cm⁻¹ indicating the high purity of carbon compound existing in singular layers stacking. This change suggests a decrease in the average size of the sp² domains upon reduction of the exfoliated GO, and can be explained, if new graphitic domains were created that are smaller in size which are present in GO before reduction and also more numerous sp² domains are absorbed in number.

A small wide hump is also observed in the region of 2D in between 2600 to 2900 cm⁻¹ which shows the presence of high crystalline single layers of graphene, but the extent of layers formed are less in quantity. The value of I_D/I_G ratio decreases from graphene oxide to graphene is shown in fig 2. (c). The G and D bands for pristine graphite is also given in (fig2. (a)).



Figure 2. G and D bands of (a) graphite (b) GO and (c) G

3.3. FTIR analysis

FTIR analysis for Graphite gives a strong and broad absorption peaks at 1134 cm⁻¹(C-O (alkoxy)), 1207cm⁻¹ (C-O (epoxy)), 1398 cm⁻¹ (C-O (tertiary)), 1535cm⁻¹ (C=C (aromatics)) skeletal vibrations; 1730 cm⁻¹ (C=O (carbonyl/carboxyl)) stretching vibrations, 3147 cm⁻¹ and 3431 cm⁻¹ due to O–H stretching vibration. These absorptions indicate the presence of all carbon II and σ bonding nature and structural stacking of K and K¹[15].

For the Graphene Oxide, the functional groups are observed at 1076 cm⁻¹ C-O (alkoxy/alkoids), $1135m^{-1}$ and $1555cm^{-1}$ C=C (skeletal vibrations), $1633cm^{-1}$ C-O bonding (skeletal vibration); $1731cm^{-1}$ C=O (stretching vibration); and $3336 cm^{-1}$ at O-H (Stretching vibration), as the graphite converts to graphene oxide. Some of the major functional group remains as of graphite, but new vibration of stretching modes and bending are formed due to high hydrophilic in nature due to the removal of oxygen functional group [16]

The functional groups of graphene are observed a broad and high strength absorption at 1066cm⁻¹ (C-O(alkoxy)), 1205cm⁻¹ (C-O (epoxy)) ;1399cm⁻¹ (C-O (carboxy)); 1715cm⁻¹ (C=O (carbonyl/carboxy) stretching vibrations) and 3132cm⁻¹(attributes to O–H stretching vibration) are due to reduction of graphene oxide on thermal treatment makes the removal of some oxygen functional group and some loose bonding of Π and σ due to thermal effect and only the main carbon/carboxy functional group shows the existing of graphite in nature in singular plane sheet are shown in the fig 3.



Figure 3: FTIR (a) Pure graphite (b) Graphene Oxide and (c) Graphene

3.4. UV analysis

The absorption spectra of GO dispersion exhibits a maximum absorption peak at about 216 nm corresponding to π - π * transition of aromatic C-C bonds and shoulder at about 230 nm ascribed to n- π * transitions of C-O bonds. The absorption peak for reduced GO is red shifted to 260 nm are also observed for higher annealed sample. The UV-Vis absorbance spectrum of the GO shows a higher transmittance of about 90 to 95%. Due to oxidation of graphite by chemical synthesis which makes the randomly arranged sp² hybrids planes into a regular periodic orientation of the respective indices create a shift in band level. Hence, it gives the change in absorbance and transmission of light from pristine graphite. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO [16].

After reduction (blue shift), the aromatic C-O bonds red shift to 196 nm and 212 nm indicating the restoration of a π -conjugation network within Graphene sheets which indicates the uniformity of sp² hybridization is well defined mono layer crystalline in nature. The graphene absorption shows at lower level absorption of 2 to 5% and higher rate of transmission up to 98 to 95% are due to single crystalline nature of sp² atomic stacking in major planes with same orientation resulting in high uniformity. The corresponding peak values are observed at 196 nm and 212 nm. The optical transmission of graphene is found to 97% confirmed by theoretical and other experimental values which are matches with the result showing a high transmittance are shown in the fig 4.



Figure 4: (a) Pure graphite (b) Graphene Oxide and (c) Graphene

3.5. SEM

Scanning Electron Microscopy images confirm morphological study of synthesized particles as a crimpled paper like structure which resembles in buds and flowers in nature for both Graphene Oxide Fig. 5(a)) and Graphene (Fig.5. (b)). It resembles like jasmine flower in nature [11].



Fig 5(a) : SEM image of Graphene Oxide



Fig 5(b): SEM image of Graphene nano particles.

4. CONCLUSION

The synthesized materials show the existence of very small particle with low crystalline for Graphene Oxide, Reduced Graphene Oxide and Graphene are confirmed from XRD data. The level of purity of carbon atoms and the absence of impurities are clearly stated by Raman. The functional analysis of the materials are characterized by the FTIR which shows the presence main compound of carbon, oxygen corresponding structural formation and bending of atomic orientations are obtained in well define high quality in manner. The optical and transmittance of the materials is characterized by the UV spectrum which gives the indication of transmission of graphene at a good level. SEM images reveal the clear structural formation for the lower size nano particle. Finally, the graphene powder shows good properties for catalysts and ultra capacitors.

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Synthesis and Study on Structural, Morphological and Magnetic properties of nanocrystalline Manganese Oxide

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Abstract: Mn_3O_4 nanoparticles were prepared by co-precipitation method followed by annealing of samples at 300 °C for 2 hours. The samples were characterized to find the structural, functional, optical, morphological, compositional and magnetic properties by PXRD, FTIR, Micro-Raman, HRSEM, TEM, XPS, EDX and VSM respectively. Structural studies by PXRD indicate that the annealing has strongly influenced the phase transition showing two coexisting phases of Mn_2O_3 and Mn_3O_4 . Micro-Raman spectra showed the presence of A_{1g} mode of vibration corresponding to Mn_3O_4 phase. Magnetic studies of the as synthesized Mn_3O_4 nanoparticles depict paramagnetic behavior at room temperature.

Keywords: manganese oxide, co precipitation, magnetic properties

1. INTRODUCTION

In recent past, considerable research attention is paid on Mn based compounds as it has many interesting properties that can be tailored for numerous applications. Mn₃O₄ is an important transition metal oxide due to its extensive applications in magnetic [1], electrochemical [2], Li ion batteries [3], catalytic applications [4], supercapacitors [5] and dilute magnetic semiconductor [6]. Mn₃O₄ nanoparticles have been synthesized in several methods like hydrothermal [7], combustion method [8], microwave assisted solution method [9], and co precipitation method [10]. In this report, we have attempted to optimize Mn₃O₄ nanoparticles by facile coprecipitation method as it is simple and cost effective technique. As synthesized nanoparticles were annealed to 300 °C and their structural, morphological, functional, compositional and magnetic properties were compared.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of Manganese Oxide Nanoparticles

All chemicals used were of AR grade and was used without further purification. A simple chemical co precipitation method was employed to synthesis Mn_3O_4 nanoparticles. 1M of $MnSO_4$. H_2O was dissolved in de-ionized water. 2M of NaOH was added drop wise to this solution and pH was maintained at 11 ± 0.2 by adding ammonia. Solution was stirred continuously under constant temperature (60 °C) for 2 hours for precipitation of nanoparticles. Then precipitated particles was collected and washed with de-ionized water 2 to 3 times and dried in hot air oven at 100 °C for 12 hours. As synthesized particles was annealed at 300 °C for 2 hours.

3. RESULTS AND DISCUSSION

3.1 Structural Studies

Figure 1 show the powder X-ray diffractograms of as synthesized and annealed nanoparticles, which reveals the presence of mixed phases of Mn_3O_4 and Mn_2O_3 . PXRD pattern of as synthesized nanoparticles show predominant peak with reflection (311) at 34.06° which indicates the presence of Mn_3O_4 phase with cubic structure, whereas annealed sample shows predominant peak with reflection (222) at 32.45° which can be assigned to Mn_2O_3 phase with cubic structure. The reflections (222) at 36.06° and (440) at 60.24° can be assigned to Mn_3O_4 phase. These values are in

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good agreement with JCPDS card # 040-732. The peaks with reflection (200) at 19°, (220) at 29°, (222) at 32.45°, (400) at 37.9°, (332) at 44.52° and (600) at 58.29° belongs to Mn_2O_3 phase with cubic structure. These peaks are well matched with JCPDS card # 89-4836. Aroused peak intensity of annealed nanoparticles is due to the increase in crystallinity. Due to annealing, there is shift in peak to (222) which is the crystallographic plane indicating the phase change to Mn_2O_3 and this may be due to oxidation of Mn_3O_4 to Mn_2O_3 begins at as low as temperature at 300°C [11-12].



Figure 1. PXRD diffractograms of as synthesized and annealed mixed phases of Mn₃O₄ nanoparticles.

The microstructural parameters like crystallite size, microstrain, dislocation density and lattice strain [13] were calculated and tabulated in tables 1&2. It is observed that the crystallite size increased for annealed nanoparticles, while the micro strain and dislocation density were decreased. This depicts increase in crystallinity of nanoparticles. Annealing has showed a significant effect in the structural properties of manganese oxide.

3.2 Compositional Studies

Figure 2 shows XPS survey spectrum scanned in the binding energy range between 0 to 1100 eV for as synthesized Mn_3O_4 nanoparticles to collect chemical composition and electronic states data at surface of the samples. Inset picture shows narrow window scan of Mn 2p state. The survey spectrum shows the presence of Mn, C and O with the presence of no other impurities. The C 1s (284.5 eV) peak was used for the calibration of the spectrum as internal reference. Electronic states of Mn 3s, O 1s, Mn 2p and Mn 3p are well matched with earlier reported values [2]. The peak at 642.7 eV can be assigned to $Mn 2p_{3/2}$ corresponding to Mn^{3+} and 48 eV can be assigned to $3p_{3/2}$ electronic state [14]. Spin orbit splitting between Mn $3p_{1/2}$ and Mn $2p_{3/2}$ is 11.8 eV which is nearer to literature reports [7].The binding energies at the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks agree well with that of reported for Mn₃O₄ indicating oxidation state for Mn [5].

Figure 3 (a&b) shows EDX spectra of as synthesized and annealed nanoparticles. It indicates the presence of Mn and O with the presence of no other impurities.

Table 1. Lattice parameters of as synthesized and annealed Mn_3O_4 nanoparticles

| Sample | Lattice Parameter (Å) | Volume (Å ³) | lattice distortio n(Å) |
|--------------------|--------------------------|-----------------------------|----------------------------------|
| | | | V - V ₀ |
| As- synthesized | 8.7566 | 671.428 | 12.92 |
| Annealed | 8.7887 | 678.850 | 20.35 |

Table 2. Microstructural parameters of as synthesized and annealed Mn_3O_4 nanoparticles

| Samples | Crystallite size (nm) D=0.9λ/βCosθ | $\begin{array}{c} \text{Dislocation} \\ \text{density}(10^{15} \\ \text{lines/m}^2) \\ \delta {=} 1/D^2 \end{array}$ | Micro strain (lines ⁻² m ⁻⁴) ε=βCosθ/4 |
|-------------------|--|--|--|
| As synthesized | 31.7 | 0.996 | 0.0011 |
| Annealed | 91.6 | 0.119 | 0.0004 |



Figure. 2 XPS spectrum of as synthesized Mn₃O₄ nanoparticles. Inset



Figure. 3 EDS spectra of (a) as synthesized and (b) annealed Mn_3O_4 nanoparticles

3.3 Functional Studies

The Raman scattering measurements were performed using the 514.5nm excitation line from Ar⁺ laser. Figure 4 (a&b) shows the micro-Raman spectra of as synthesized and annealed nanoparticles respectively. As synthesized nanoparticles exhibits three phonon peaks at (doubly degenerate) T_{2g} symmetry mode at 366 cm⁻¹, E_g symmetry mode at 320 cm⁻¹ and a single degenerate A_{1g} symmetry mode at 654 cm⁻¹. The band corresponding to 654 cm⁻¹ is very close to 655cm⁻¹ which is due to the stretching vibration of Mn-O in Mn₃O₄ [7]. Annealed nanoparticles shows four phonon peaks same as synthesized particles with one extra band T_{2g} symmetry mode at 487 cm⁻¹ which may be due to the out of plane bending mode of Mn2O3 phase. Presence of mixed phase of Mn₂O₃ and Mn₃O₄ is confirmed from these peaks. Also peak intensity of annealed nanoparticles is lesser than that of as synthesized particles. This may be due to increase in crystallite size for annealed nanoparticles which can be explained using phonon confinement effect as reported earlier by Jian Zuo et al [27].



Figure. 4 Raman spectra of (a) as synthesized and (b) annealed Mn₃O₄ nanoparticles.

FTIR spectra for as synthesized and annealed nanoparticles are shown in figure 5(a&b). In the region 400 to 700 cm⁻¹, the bands observed at 429 cm⁻¹, 458 cm⁻¹, 513 cm⁻¹ and 609 cm⁻¹ corresponds to the Mn-O vibrations ascribed to the stretching modes of octahedral and tetrahedral sites of Mn_3O_4 [16]. The bands at 1110 cm⁻¹ and 1633 cm⁻¹ are due to the O-H bending vibrations along with Mn [17].The broad absorption peak at 3443 cm⁻¹ indicates the presence of hydroxide group. Annealed nanoparticles exhibits an extra peak observed at 995 cm⁻¹ which may be attributed to M=O vibration of Mn_2O_3 .

3.4 Morphological Studies

HRSEM micrographs of as synthesized and annealed nanoparticles are shown in figure 6(a-c & d-f), which shows irregular shaped disk like morphology with average particle size of about 155 nm. Annealed nanoparticles also exhibit similar morphology with average particle size of about 400 nm.



TEM micrograph (figure 7) of as synthesized nanoparticles was also taken as supporting information. It confirms similar morphology with particle size of 155 nm.



Figure 7. TEM micrographs of as synthesized Mn₃O₄ nanoparticles

3.5 Magnetic studies

Magnetic behaviors of as synthesized and annealed Mn_3O_4 nanoparticles are shown in figure 8. This magnetic study was carried out in room temperature with maximum magnetic field at 15 KOe. Both as synthesized and annealed Mn_3O_4 nanoparticles exhibit paramagnetic behavior. The maximum magnetizations observed were 0.2864 emu/g and 0.5347 emu/g for as synthesized and annealed nanoparticles at maximum field. Magnetic ordering of annealed samples is increased with increase in crystallinity of the samples. [19]



Figure 8. Room temperature magnetization curves of as synthesized and annealed Mn₃O₄ nanoparticles

4. CONCLUSION

Mn₃O₄ nanoparticles were synthesized by co-precipitation method and their annealing effect was reported. PXRD revealed mixed phases of Mn₃O₄ and Mn₂O₃. Annealing of nanoparticles at 300 °C has favored the growth orientation towards Mn₂O₃ phase due to oxidation of Mn₃O₄. Increased peak intensity and decreased microstrain and dislocation density indicates the increase in crystallinity for annealed samples. XPS spectra proved the presence of Mn and O with presence of no other impurities. EDS also confirmed the composition of the samples. HRSEM micrographs showed irregular shaped plates with average particle size of 155 nm for as synthesized particles and 400 nm for annealed particles. TEM micrograph further confirmed similar morphology with particle size almost same as 155 nm. Functional studies were carried out using micro Raman and FTIR. Various bending and stretching modes of Mn-O and O-H groups were analyzed from these spectroscopic studies. Room temperature magnetic studies confirmed that the paramagnetic behavior of Mn₃O₄ nanoparticles improved for annealed samples due to increase in crystallinity.

Figure. 5 FTIR spectra of (a) as synthesized and (b) annealed Mn₃O₄ nanoparticles



Figure 6. SEM micrographs of (a-c) as synthesized and (d-f) annealed Mn₃O₄ nanoparticles

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Surfactant Assisted Growth and Optical Studies of NiCo₂O₄ Nanostructures through Microwave Heating Method

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Abstract: A fast and facile method has been imposed for the preparation of NiCo₂O₄ nanostructures using metal nitrate as a precursor material and CTAB as a surfactant. The prepared samples were characterized by Powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM), Raman and PL spectroscopy. It was found that the synthesis route proposed in this work favored the formation of NiCo₂O₄ spinel phase at low temperature. The surfactant CTAB was chosen to control over the nucleation, growth and agglomeration nature of observed NiCo₂O₄ nanocrystalline products. With the effect of surfactant, the obtained NiCo₂O₄ has been used for various promising potential applications. Based on the observed experimental observations and analysis, a possible microwave reaction mechanism is proposed to synthesis NiCo₂O₄ nanostructured materials to enrich the structural, morphological and optical properties of NiCo₂O₄ nanostructures.

Key Words: Nanostructures, X-ray diffraction, Crystal structure, Surfactant, Optical.

1. INTRODUCTION

The presence of two metals in the same molecule largely affects both the physical and chemical properties and it has wide range of applications in various fields like electrocatalysts, chemical sensors, magnetic and biomedical applications [1]. The binary cobaltites of transition metals with the general formula MCo₂O₄, where M is a divalent cation of a d element, Ni, Cu and Zn cobaltites are of definite interest due to their significant modification in the individual properties of the metals which do not occur in monometallic compounds [2]. Nickel cobaltite (NiCo₂O₄) is one of the important metal oxides in the family of cobaltite materials which has a spinel structure AB₂O₄. Basically the incorporation of nickel ion into cobalt oxide would strongly enhance the properties of the prepared samples towards many applications [3]. In the recent years, large number of chemical methods were adopted and used for the preparation NiCo₂O₄ nanoparticles such as sol-gel process [4], co-precipitation [5], microwave [6], solid state [7] and solvothermal [8]. Recently, the microwave method has been most widely used for NiCo₂O₄ nanoparticles because of effectiveness of fast reaction and shorter heating time. In this paper, we report that the effect of calcination temperature on structural, optical, morphological and compositional analysis of nanocrystalline NiCo₂O₄ powders by a fast and facile microwave method using CTAB as a surfactant. This process is an effective way to produce nanoparticles with enhanced properties by using the effectiveness of CTAB towards various applications.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Nickel Cobaltite

Nickel cobaltite (NiCo₂O₄) was synthesized from microwave reaction using the precursor materials of Co (NO₃)₂.6H₂O, Ni (NO₃)₂.6H₂O and the surfactant CTAB. In this reaction, 3 g of Ni (NO₃)₂.6H₂O was added to the 50 ml distilled water. Then 6g of Co (NO₃)₂.6H₂O was mixed with nickel nitrate solution and 2.5 g of CTAB was added to the precursor solution. Finally 3ml of ammonia was added to maintain the pH value around 9-10.

The solution was treated with microwave reaction with the power of 180 W in 15 min. The precipitate was collected and dried at hot air oven with 80 $^{\circ}$ C for 24 hours. Then the powder was calcined at different temperatures namely 400 $^{\circ}$ C, 600 $^{\circ}$ C and 800 $^{\circ}$ C

3. RESULTS AND DISCUSSION

3.1. Structural and Functional Analysis

Figure 1A(a1-a3) shows the XRD patterns of NiCo₂O₄ spinel structure calcined at three different temperatures such as 800 °C, 600 °C and 400 °C respectively. Characteristic diffraction lines of the NiCo2O4 spinel structure were well matched with standard JCPDS (73-1702) in all calcined samples [9]. The peaks related to NiO phase were also identified from the XRD spectrum. It was observed from the XRD patterns that the crystallite size grows when the calcination temperature increases. At higher calcinations of 800 °C shown in figure A (a1), crystalline nature was increases compared to lower calcination temperatures. It is strongly concluded that, the formation of NiCo₂O₄ at lower calcination temperature is less and it increases with higher calcination temperature with increasing particle size. The lattice parameters were calculated and tabulated in table 1. The FTIR spectra of the NiCo₂O₄ nanoparticles were displayed in figure 1B(b1-b3) for three calcined samples. In this analysis, two strong absorption bands in the region 650-665 cm⁻¹ and 550-560 cm⁻¹ corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are the characteristics of cobaltites. Only the Co-O and Ni-O vibrations of NiCo₂O₄ samples are detected, no signal corresponding to OH group is observed, indicating the cobalt and nickel metallic salts are completely decomposed after calcination. The peak positions were shifted to higher side with respect to increase of calcination temperatures. No other peaks were obtained in the FTIR spectrum indicates that the purity of NiCo₂O₄ nanoparticles is good without other species in the samples [10&11].



Figure 1. A) X-ray diffraction pattern of NiCo₂O₄ for a1) 800 °C, a2) 600°C and a3) 400°C, B) FTIR spectra for b1) 800 °C, b2) 600°C and b3) 400°C respectively and C) Comparison graph of particle size and lattice parameter.

Figure 1C gives the comparison of particle size, lattice constant variation with the calcination temperatures. It is observed from the figure that, increase of calcinations temperature increases the particle size but lattice constant is found to be decreased.

| Calcination Temperature (° C) | Grain Size(nm) | Dislocation Density 10 ¹⁴ lines/cm ² | Lattice constant (a) Å | Volume (V) (Å) ³ | Lattice distortion (V ₀ -V) |
|----------------------------------|-------------------|---|---------------------------|-----------------------------|---|
| 400 | 16.75 | 0.3563 | 8.0934 | 530.15 | 0.0076 |
| 600 | 44.10 | 5.1451 | 8.0909 | 529.65 | 0.0085 |
| 800 | 55.90 | 3.2056 | 8.0788 | 527.28 | 0.0129 |

| 1 able 1. Structural parameters of NiCo ₂ O ₄ calcined at three different temperatures | Table 1. | Structural | parameters | of NiCo ₂ | O4 calcined | at three | different | temperatures. |
|--|----------|------------|------------|----------------------|-------------|----------|-----------|---------------|
|--|----------|------------|------------|----------------------|-------------|----------|-----------|---------------|

3. Morphological and Compositional Analysis

The morphological variations of NiCo₂O₄ spinel structure with the effect of calcination temperatures are shown in Figure 2. The images of NiCo2O4 calcined at 400 °C displayed highly agglomerated nanoparticles (Fig.2 (a&b)). When the calcination temperature increases to 600 °C, (Figure 2(c & d)), particles are formed into irregular quasi spherical shape with increasing size. In further increase of calcination temperature (800 °C), particles are grown into uniform morphology with spherical shape shown in figure 2 (e&f). The particles size obtained from higher calcined sample is in the range of 50-100 nm which is higher than lower calcinated samples. By increasing the calcination temperature, the shape of particles is changed into uniform size with better morphology which is clearly observed in the SEM micrographs. EDS analysis were performed to identify the elemental composition of NiCo₂O₄ nanoparticles and the corresponding images are displayed in figure 3(a-c) for the different calcinated samples.



Figure 2. Low and high magnification SEM images of NiCo₂O₄ nanoparticles for 400 $^{\circ}$ C (a&b), 600 $^{\circ}$ C (c&d) and 800 $^{\circ}$ C (e&f) calcinated samples



Figure 3. EDAX spectra of NiCo₂O₄ nanoparticles for a) 400 °C, b) 600°C and c) 800°C calcinated samples.

3.3 Optical Analysis

The photoluminescence spectrum of NiCo₂O₄ nanoparticles is shown in figure 4(a-c) for the corresponding calcination temperatures of 400 °C, 600 °C and 800 °C. This spectrum displayed two strong emission peaks at 360 and 490 nm for all the three samples with increasing peak intensity with calcination temperatures. The band gap energies of the NiCo₂O₄ nanoparticles are calculated and it gives 3.45 eV and 2.53 eV for the corresponding emission peaks of 360 and 490 nm [12].



Figure 4. PL spectra of NiCo_2O_4 nanoparticles for a) 800 $^\circ C,$ b) $600^\circ C$ and c) 400 $^\circ C$ respectively

In order to further understand the composition and structure of these NiCo₂O₄ samples, Raman spectrum was taken which is shown in Figure 5. With respect to the as-prepared NiCo₂O₄ samples, the peaks at 152, 455.2, 505.2, 657.2 and 1097.3 cm⁻¹ correspond to F_{2g} , E_g , LO, A_{1g} and 2LO modes of NiCo₂O₄, respectively. These results are well consistent with previously reported literatures [13&14].





Figure 5. Raman spectra of NiCo_2O_4 nanoparticles for a) 800 $^\circ C$, b) 600 $^\circ C$ and c) 400 $^\circ C$ calcinated samples

4. CONCLUSION

It was found that the microwave route proposed in this work favored the formation of NiCo₂O₄ spinel phase confirmed from the X-ray diffraction with increasing particle size with calcination. It produced uniform spherical shaped particles at higher calcination with size around 50-100 nm than other low temperature calcinated samples. EDS results confirmed the presence of elements Co, Ni and O in NiCo₂O₄. PL results showed that the band gap of NiCo₂O₄ nanoparticles are 3.45 and 2.53 eV and Raman spectrum emerges the Co–O and Ni–O vibrations in NiCo₂O₄ samples. The calcination effect was used to study the nucleation, growth and agglomeration nature of NiCo₂O₄ nanoparticles with the effect of surfactant CTAB. The uniform sized NiCo₂O₄ can be used for various promising potential applications.

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Effect of Solvents on Size and Morphologies Of sno Nanoparticles via Chemical Co-precipitation Method

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Abstract: Stannous oxide (SnO) is an important functional material which contributes to a wide range of applications. In present study, the SnO nanoparticles were synthesized using different solvents by chemical co-precipitation method. Different morphologies of SnO nanoparticles have been obtained by different solvents. The size of SnO nanoparticles was estimated by powder X-ray diffraction (PXRD) pattern and revealed that SnO crystallizes into tetragonal rutile phase. The chemical structural information of the synthesized nanoparticles was studied by Fourier transform infrared (FTIR) spectroscopy. The prominent UV emission peak was observed at 358 nm in the luminance spectra, studied by photoluminescence (PL) spectroscopy. The composition of the product SnO nanoparticles could be determined by X-ray photoelectron spectroscopy (XPS) and the binding energies of O 1s and Sn 3d_{3/2} have been found which are centered at 530 and 495 eV, respectively.

Keywords: Stannous oxide; semiconductor; nanoparticles; morphologies; co-precipitation

1. INTRODUCTION

Nanostructured materials have attracted great interest in both fundamental as well as applied research areas due to their outstanding physical and chemical properties and also promising applications in nanodevices [1]. A reduction in particle size to nanometer scale results in various interesting properties compared to the bulk properties. Stannous oxide (SnO) is one of the best p-type semiconductors found in literature for various applications. The naturally formed tin (Sn) vacancies causes the variable direct band gap in SnO, has attracted considerable attention owing to its specific functional characteristics and significance in a various technological applications such as coating substrate, catalyst, thin film transistors, etc.[2]. Variety of solution phase techniques like homogeneous co-precipitation [3]. hydrothermal route [4], sol gel method [5], sol gel combustion [6], mechanical ball milling [7], and sonochemical method [8] have been employed to synthesis metal oxides. Among these, co-precipitation method is a simple and less expensive and requires simple instrumentation. A variety of SnO distinct morphologies have been successfully synthesized such as particle, platelet [9], flower [10], whiskers [11] and dendrites [12]. However, the implementation of nanostructure's preparation of SnO with well controlled size and morphology by chemical co-precipitation method is a great challenge for nanomaterials synthesis. Here, we report the size and morphological changes of SnO nanoparticles using different solvents. The properties of as-synthesized SnO nanoparticles were determined by using XRD, FTIR, SEM, PL and XPS.

2. EXPERIMENTAL DETAILS

In the synthesis process, all reagents of analytical grade (AR) were used without further purification. 0.36M of tin chloride $(SnCl_2)$ was dissolved in different solvents such as de-ionized water, ethanol, ethylene glycol and propanol. Then, NaOH solution was added drop wise into the solution to maintain the pH of solution between 8-11. The resultant solution was stirred constantly for 60 minutes and then after vigorous stirring, white suspension was obtained. The product was centrifuged, filtered out and rinsed with alcohol and deionized water several times to remove soluble impurities if any in the

solution, and then dried at 60°C for 1h in air atmosphere, and finally the product was collected for characterization.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

The PXRD patterns of synthesized SnO nanoparticles using different solvents are shown in figure 1. The diffraction peaks are well matched with the standard SnO reflections (JCPDS Card No. 06 - 0395).



The X-ray pattern reveals that SnO nanoparticles are having tetragonal wurtzite structure and the obtained peaks are indexed to (001), (101), (110), (002), (200), (112) and (211) planes. The reduction in peak intensities and broad FWHM were observed for the samples synthesized in solvents of ethanol and propanol. The calculated values of grain size, dislocation density and strain are tabulated in table 1.

| SI. No | Solvent | Grain Size D=0.9λ/ βcosθ (nm) | $Dislocation \\ Density \\ \delta = 1/D^2 \\ (lines/m^2)$ | $\begin{aligned} & \text{Micro} \\ & \text{Strain} \\ & \epsilon = \beta \\ & \cos\theta / 4 \\ & (\text{lines}^{-2}/\text{m}^4) \end{aligned}$ |
|-----------|--------------------|---|---|---|
| 1. | Water | 40.83 | 0.599 E+15 | 0.849 E-03 |
| 2. | Ethanol | 13.61 | 5.3982E+15 | 2.547 E-03 |
| 3. | Ethylene Glycol | 8.17 | 14.980E+15 | 4.243 E-03 |
| 4. | Propanol | 6.81 | 21.584E+15 | 5.093 E-03 |

 Table 1. Grain size and micro structural parameters of SnO nanoparticles

3.2 Functional Analysis

FTIR spectrum is a useful tool to understand the functional groups of any organic molecule. The FTIR spectra of SnO nanoparticles collected using different solvents are shown in Figure 2. Metal oxides generally give absorption band below 1000 cm⁻¹ arising from inter-atomic vibrations.



Figure 2. FTIR spectra of SnO nanoparticles

For all synthesized products, the absorption peaks are found at 3456 and 1618 cm⁻¹ are attributed mainly to the O-H stretching vibration of surface hydroxyl group or adsorbed water of the SnO nanoparticles [13]. The principal peak observed at 1586 cm⁻¹ corresponds to the strong asymmetric stretching of C=O bond. The presence of N-O is conformed from the peak observed at 1409 cm⁻¹. The absorption band at 515 cm⁻¹ is ascribed to the terminal oxygen vibration of SnO [14].

3.3 Morphological Analysis

Figure 3 shows the SEM micrograph of SnO using different solvents. The formation of plate like morphology is obtained using water as a solvent and it produces better morphology than the other solvents like ethanol, ethylene glycol and propanol. The formation of SnO nanoparticles are highly agglomerated for other solvents because of the formation of

smaller particles. But for the case of water solvent, the size becomes higher and it produces less agglomerated particles.



Figure 3. SEM images of SnO nanoparticles using different solvents

3.4 Photoluminescence studies

Figure 4 shows the room-temperature photoluminescence spectra collected by using an excitation wavelength of 325 nm. A strong UV emission peak located at 358nm (3.4 eV) corresponding to the near band-edge emission observed for all samples. The propanol mediated sample gives a very prominent UV emission. However, ethanol, ethylene glycol and water mediated samples show less intense UV emission peak comparable with the propanol mediated sample. Huan-Ming Xiong et al reported the surface state is regarded as a main factor that determines SnO visible luminescence, because SnO visible emission arises from its defects or vacancies which mainly located on the nanoparticles surface [15].





3.5 Compositional Analysis

Figure 5 shows the high resolution XPS spectra of assynthesized nanoparticles. The dominant signals corresponding to $Sn3d_{5/2}$, $Sn3d_{3/2}$ and O1s are found at 486.2, 495.4 and 530.7eV respectively. These values are matching well with the previous reports for SnO [16]. The O1s photoelectron peak is observed at 530.7 eV revealed that oxygen atoms are bonded to the Sn atoms.



Figure 5. XPS spectra of SnO nanoparticles

4. CONCLUSION

Controllable size and different morphologies of SnO nanoparticles have been synthesised using different solvents by co-precipitation method. The size of the SnO nanoparticles has been estimated by PXRD. The chemical structural information of the product SnO has been studied by FTIR spectra. The different solvents give various morphologies studied by SEM analysis. The intensity of UV emission peaks are found to be varied with respect to the solvents used. The composition of the SnO nanoparticles has been determined by X-ray photoelectron spectroscopy (XPS).

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Box-Behnken Experimental Design for the process optimization of Strontium substituted Hydroxyapatite synthesis

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Abstract: Hydroxyapatite is the major mineral constituent of vertebrate bones and teeth can significantly increase the biocompatibility and bioactivity of man-made biomaterials. Strontium substituted Hydroxyapatite, a bioceramic was successfully synthesized by solution combustion method using calcium acetate and diammonium hydrogen orthophosphate as precursors. Statistical Design of experiments was employed as a tool for systematic evaluation and investigation of the influencial process variables. Limited research was found on combustion synthesis of Sr substituted hydroxyapatite. The main objective of this work is to understand the effects of three important process parameters, synthesis time, ignition temperature and % Sr substitution on the resulting yield and crystallite size. Contour plots were generated to study the interaction between these factors. A specific approach based on Box-Behnken design was used to evaluate these parameters and to optimize them for a more effective synthesis. Mathematical models were developed for each of the measured responses yield and crystallite size. The adequacy of the developed model was checked using analysis of variance technique and experimental validation. It has been observed that all the three parameters significantly affect the response variables. The maximum yield can be obtained when the synthesis is done at 500°C for 30 minutes and the crystallite sizes increases with the % Sr substitution.

Keywords: Hydroxyapatite, Strontium, Design of Experiments, Box-Behnken, optimization, yield, crystallite size

1. INTRODUCTION

Calcium phosphate ceramics such as hydroxyapatite [Ca10 (PO₄)₆(OH) 2] is one of the most effective biocompatible material and is found to be the major component of the bone. This material is the most promising implant coating materials for orthopedic and dental applications due to their good biocompatibility. The superior biocompatibility of calcium phosphates contributed by their compositional resemblance with the bone mineral has allowed them to be used [1]. The greatest potential for bone substitution is shown by materials based on hydroxyapatite (HAp), which can develop tight bonding with bone tissue, exhibits excellent biocompatibility, osteoconductive behavior, is stable toward bioresorption, and has no adverse effects on the human organism [2]. Synthetic HAp nanoparticle is similar in crystal lattice to natural bone and can be used as bone substitute or dental enamel remineralization material. However, synthetic pure HAp nanoparticle has some shortcomings, such as the weak antibacterial property, the high degree of crystallinity and the stability of the structure, which lead to low biodegradation and poor effect for implant use or dental care use [3]. Therefore, it is necessary to improve its properties to use it as biomaterial. Incorporation of metal ions into the HAp structure can improve the properties of HAp, metal ions such as Ag⁺, Cu²⁺ in the structure can affect its solubility, crystallinity, morphology and lattice parameters, and even improve its antibacterial property. Strontium (Sr) is one of the essential trace elements in human body, which can enhance the strength of bone and prevent caries. Sr and Ca share the same group in the periodic table of elements, Sr may replace Ca to form Strontium substituted hydroxyapatite, resulting in the improvement of solubility and Biodegradability [4-8]. Strontium can replace calcium in hydroxyapatite, and hence in bone, without much difficulty. It is reported that the stable strontium is non-toxic even when it is administered in large doses in our body for prolonged periods.

Many researchers reported on the preparation methods of Strontium substituted Hydroxyapatite (Sr-HAp) nanoparticles are sol-gel, precipitation and hydrothermal, by which the nanoparticles usually need to be calcined to improve the crystal structure at a high temperature of about 900°C, which may cause the nanoparticles to decompose. However solution combustion synthesis is a suitable method to produce Sr-HAp powder at a low ignition temperature. The aim of this work is to examine the influence of process parameters on synthesized Sr-HAp properties and determine an optimum set of process variables to produce Sr-HAp powders of desired characteristics. Design of Experiments (DoE) is employed to investigate the influencial process variables of combustion synthesis and to optimize them. From the literatures, the following observations have been made: (i) The initial furnace/ignition temperature was found to be a very important reaction parameter. The lower value of furnace temperature was selected as 400°C and the upper value as 600°C. (ii) time for the reaction was also considered as another major factor for the complete transformation to HAp (iii) the lower and upper limits of substitutions selected in this experiment are 0 and 30% Sr into hydroxyapatite.

2. MATERIALS AND METHODS

Response surface methodology is a collection of statistical and mathematical method that are useful for the modeling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. Response surface methodology also quantifies the relationship between the controllable input parameters and the obtained response surfaces [9-10]. The design procedure of response surface methodology is as follows: (i) Designing of a series of experiments for adequate and reliable measurement of the response of interest, (ii) Developing a mathematical model of the second order response surface with the best fittings, (iii) Finding the optimal set of experimental parameters that produce a maximum or minimum value of response, (iv) Representing the direct and interactive effects of process

parameters through two and three dimensional plots. The factors are investigated at three levels +1 (high), 0 (middle) and -1 (low). The percentage Sr substitution, ignition temperature and synthesis time are taken as the important influential process variables and tabulated in Table 1. These are evaluated against yield and crystallite size of the produced Sr-HAp. If all variables are assumed to be measurable, the response surface can be expressed as follows,

$$Y = f(x_1, x_2, x_3, \dots, x_k)$$
 (Eq.1)

where y is the answer of the system, and xi the variables of action called factors. The goal is to optimize the response variable y. It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between independent variables and the response surface. Usually a second-order model is utilized in response surface methodology.

$$Y = b_0 + \sum b_i X_i + b_{ij} X_i X_j + b_{ii} X_{ii}^2 + \mathcal{E}, \quad (Eq.2)$$

Where i, j vary from 1 to number of process variables, coefficient b_0 is the mean of responses of all the experiment, b_j coefficient represents the effect of the variable X_i and b_{ij} , are the coefficients of regression which represent the effects of interactions of variables X_iX_j and b_{ii} , are coefficients of regression which represent the effects of regression which represent the effects of interactions X_iX_j and \mathcal{E} is the experimental error, such that

Where Y_1 is the response 1, b1-b9 is the regression coefficient, A is the strontium substitution, B is the ignition temperature and C is the synthesis time. This model was used to evaluate the same responses (Y1, Y2), such as Y1 the yield (%) and Y_2 the crystallite size (nm). The design matrix of experiments, in real values obtained according to the optimized Box-Behnken design, as shown in Table 1. The three key controllable process parameters (Strontium substitution, ignition temperature and synthesis time) were selected; these factors were investigated at three levels: strontium substitution (0 %, 15 %, and 30 %), ignition temperature (400 °C, 500 °C, and 600 °C), synthesis time (20 min, 30 min, 40 min). Each factor level represented minimum (-1), centrepoint (0), and maximum values (+1), respectively. Therefore 17 experimental runs were conducted in Box-Behnken design.

3. RESULTS AND DISCUSSION

The factors and the responses from the results of the synthesized powders with Box-Behnken experimental design are presented in Table 1. Analysis of the regression coefficients of the quadratic polynomial models describing the relationship between the responses of yield and crystallite Size against the three factors (A, B, C) are presented in the following sections.

Table 1. Box-Behnken design trial experiments

| | Factor 1 | Factor 2 | Factor 3 | Respo nse 1 | Respons e 2 |
|---------|--------------------------|-------------------|----------|----------------|----------------------|
| Exp. No | A:Sr Substitut ion | B:Temp erature | C:Time | Yield | Crystalli te Size |
| | % | °C | min | % | nm |
| N1 | 0 | 400 | 30 | 26 | 14 |
| N2 | 30 | 400 | 30 | 23 | 38 |
| N3 | 0 | 600 | 30 | 33 | 22 |
| N4 | 30 | 600 | 30 | 28 | 49 |
| N5 | 0 | 500 | 20 | 30 | 10 |
| N6 | 30 | 500 | 20 | 25 | 40 |
| N7 | 0 | 500 | 40 | 29 | 23 |
| N8 | 30 | 500 | 40 | 26 | 50 |
| N9 | 15 | 400 | 20 | 22 | 16 |
| N10 | 15 | 600 | 20 | 29 | 23 |
| N11 | 15 | 400 | 40 | 25 | 45 |
| N12 | 15 | 600 | 40 | 21 | 57 |
| N13 | 15 | 500 | 30 | 36 | 33 |
| N14 | 15 | 500 | 30 | 36 | 33 |
| N15 | 15 | 500 | 30 | 36 | 33 |
| N16 | 15 | 500 | 30 | 36 | 33 |
| N17 | 15 | 500 | 30 | 36 | 33 |
| | | | | | |

3.1 Yield Model Development

The 2D surface and 3D contour plots illustrated in Figure 1 and 2 examine the effects of the two significant factors (ignition temperature and synthesis time) on the yield response. The results indicate that both the ignition temperature and the synthesis time exert a significant effect on the response for phase purity. It is clear that strontium substitution at 15 % results in marked increase in the yield.



Figure. 1 Interaction between process parameters for yield



Figure. 2 3D graphs on interaction for yield

The maximum yield of 36.1541 occurs at a ignition temperature of 500^{0} C and synthesis time of 30 min. at a strontium substitution of 15 %. As a result of analyzing the measured responses using the Design Expert software, the test for significance of the regression models and the test for significance on individual model co-efficient were performed using the same statistical software package for all responses. By selecting the stepwise regression method, the insignificant model terms (P<0.05), were automatically eliminated. The resulting ANOVA table (Table 2) for the reduced linear phase purity model outlines the analysis of variance for this response and show the significant model terms affecting the yield.

Table 2 ANOVA Results for quadratic model

| | Sum | Mean |
|-------------------|---------|----------------------------|
| Source | of | df squares F-value R-value |
| | squares | |
| Model | 442.68 | 6 73.78 40.15 <0.0001 |
| A-Sr substitution | 32.00 | 1 32.00 17.41 0.0019 |
| B-Temperature | 28.13 | 1 28.13 15.31 0.0029 |
| B*C | 30.25 | 1 30.25 16.46 0.0023 |
| A ² | 29.01 | 1 29.01 15.79 0.0026 |
| B ² | 145.33 | 1 145.33 79.09 <0.0001 |
| C^2 | 145.33 | 1 145.33 79.09 <0.0001 |
| Residual | 18.38 | 10 1.84 |
| Lack of fit | 18.38 | 6 3.06 |
| Pure error | 0 | 4 0 |
| Cor Total | 461.06 | 16 |

 $R^2 = 0.9601$, Adj. $R^2 = 0.9362$, Pred. $R^2 = 0.7674$, Adeq. Precision = 18.825

This table also shows other adequacy measures, such as, R^2 , Adjusted R^2 and Predicted R^2 . All the adequacy measures should converge close to 1, which is in reasonable agreement in indicating adequate models. The adequate precision in this case is 18.825. An adequate precision ratio of greater than 4 indicates adequate model discrimination. The analysis of variance, indicates, that for the yield model, two of the combustion synthesis parameters have an effect on the resulting yield model, either as a main or interaction effect with another parameter. The main effects of the strontium substitution(A), ignition temperature (B) and the quadratic effects of ignition temperature*synthesis time (B*C), strontium substitution (A²), ignition temperature (B²) and synthesis time (C²) are the most significant model terms associated with yield. The final mathematical models in terms of coded factors, as determined by the design expert software are shown in Equation 4.

Yield =
$$36 - 2*A + 1.88 * B - 2.75 * (B*C) - 2.65 * A^2$$

- $5.88 * B^2 - 5.87 * C^2$ (Eq.4)

3.2 Crystallite size model development

Figure 3 and 4 shows the 2D and 3D contour graphs, highlighting the significant interaction effect between the strontium substitution and ignition temperature at synthesis times of between 20 to 40min.



Figure. 3 Interaction between process parameters for crystallite size

It is clear from this figure that an increase in the synthesis time produces a marked increase in crystallite size, while a reduction in the synthesis time appears to favour this response. A low value (20 min) of synthesis time also appears



Figure. 4 3D surface graphs for interaction between process parameters

to favour an decrease in crystallite size. As a result of analyzing the measured responses using the same statistical software used for this study, the fit summary output indicated that for the response concerning crystallite size, the quadratic model is statistically recommended for further analysis as this has the maximum predicted and adjusted \mathbb{R}^2 . The test for significance of the regression model, the test for significance on individual model coefficients and the lack of fit test were performed for this response. By selecting the step-wise regression method, the insignificant model terms were automatically eliminated. The resulting ANOVA table (Table 3) for the reduced quadratic models outline the analysis of variance of each response and show the significant model terms.

Table 3 ANOVA Results for quadratic model

| Source | Sum of squares | 3 | Mean df squares | s F-value | R-value |
|-------------------|----------------------|----|--------------------|-----------|----------|
| Model | 2563 | 3 | 854.33 | 40.05 | < 0.0001 |
| A-Sr substitution | 1458 | 1 | 1458 | 69.88 | < 0.0001 |
| B-Temperature | 180.5 | 1 | 180.5 | 8.65 | 0.0115 |
| C-Time | 924.5 | 1 | 924.5 | 44.31 | < 0.0001 |
| Residual | 271.24 | 13 | 20.86 | | |
| Lack of fit | 271.24 | 9 | 30.14 | | |
| Pure error | 0 | 4 | 0 | | |
| Cor Total | 2834.24 | 16 | | | |

 $R^2 = 0.9043$, Adj. $R^2 = 0.8822$, Pred. $R^2 = 0.8002$, Adeq. Precision = 21.889

The same table show also the other adequacy measures R^2 , Adjusted R^2 and Predicted R^2 , with an Adequate Precision Ratio of 21.889, to indicate adequate model discrimination was achieved and shows that elimination quadratic terms did not have an influence on attaining a significant model. The order of significance for these effects follows the order: C >A>B. Final model in terms of coded factors is shown in Equation (5).

 $Crystallite \ size = \ \ 32.47 \ + \ 13.5 \ ^* \ A + \ 4.75 \ ^* \ B \ + \ 10.75 \ ^* \ C \ \ (Eq.5)$

The three process parameters have a slightly positive effect on the crystalline size. It is evident that positive linear relationship of these three process parameters increases the crystallite size. Increase in the value of the process parameters increases the crystallite size.

3.3 Optimization

The above equation 5 indicates that the order of the level of significance of the positive effects of the combustion synthesis process parameters on the crystalline size follows

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the order: (C) > (A) > (B), while there is no negative effects of the combustion synthesis process parameters.



Figure. 5 Effect of the process parameters on the crystallite size

The perturbation plot aids in comparing the effect of all the factors at a particular point in the design space. Figure 3 shows a comparison between the effects of strontium substitution, ignition temperature and synthesis time on the minimum crystalline size.

4. CONCLUSIONS

The three level factorial Box-Behnken design was applied to study the two responses in synthesis of Sr-HAp by solution combustion method. Strontium substitution and ignition temperature were significantly affect final yield for experimental conditions. Strontium substitution, ignition temperature and synthesis time were significantly affect final crystallite size for experimental conditions. Sr-HAp possessing optimum powder characteristics can be prepared using the following solution combustion process parameters: Strontium substitution can be carried out at the ignition temperature of about 500°C for a synthesis time of 30 min. to get maximum yield having a nano range crystallite size.

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EVALUATING STRUCTURAL, OPTICAL & ELECTRICAL CHARACTERIZATION OF ZINC CHALCOGENIDES - FP - LAPW+ IO METHOD

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Abstract: To evaluate the structural, optical & electrical properties of the zinc chalcogenides (ZnO, ZnS, ZnSe & ZnTe), the Full Potential Linearized – Augumented Plane Wave plus Local Orbits (FP - LAPW+lo) method. For the purpose of exchange-correlation energy (E_{xc}) determination in Kohn–Sham calculation, the standard local density approximation (LDA) formalism has been utilized. Murnaghan's equation of state (EOS) has been used for volume optimization by minimizing the total energy with respect to the unit cell volume. With the result of electronic density of states (DOS), the structural, optical and electrical properties of Zinc chalcogenides have been calculated. The second derivative of energy, as a function of lattice strain has been successfully used to estimate the elastic constants of these binary compounds. The results are in good agreement with other theoretical calculations as well as available experimental data.

Keywords: Semiconductors, Chalcogenides, Density Functional Theory, FP-LAPW+lo, Electric properties,.

1. INTRODUCTION

The World of Physics pays much attention to investigate and understand the properties of solids. Because of the high difficulties in experimental work, high cost of chemicals, results accuracy and time consumption researchers are now choosing the theoretical methods. Density Functional Theory (DFT) [1] gives the exact solution to calculate the groundstate properties of all kind of materials. This theory helps to investigate and study the physical properties like electrical, elastic, mechanical, optical, magnetic, thermal and structural of materials. Modern high configuration computer helps researchers to evaluate the physical properties by using this theory.

It is very important to study the band gap and Density of States (DoS) in semiconducting materials. Because of the modern devices and applications are completely based on the band gap and optical absorption. The band structure of ZnX binary compounds have been calculated by using Full Potential Linearized Augmented Plane Wave method Plus local orbits (FP-LAPW+lo) within the Generalized Gradient Approximation (GGA). Many researchers studied the optical parameters of Zinc chalcogenides ZnX (X= S, Se, and Te) belong to II-VI semiconductors [2-8]. There are several methods and theoretical reports available to calculate the band structure and optical properties but some controversies are at there. But the FP-LAPW+lo gives the closer values with the experimental data.

The variation in energy gap is completely based on the method to calculate the band structure. Some theoretical reports are in good agreement with the measured one. They were calculated based on Local Density Approximation (LDA). But we have used FP-LAPW+lo to calculate the band structure. Our values are in good agreement with the earlier reports.

The aim our work is to evaluate the structural, electronic, optical and thermal properties of ZnX binary compounds. FP-

LAPW+lo is the method used to investigate the properties and the values are compared with the experimental and other theoretical works for these compounds.

The rest of the paper is organized as follows. After a brief introduction in section 1, the calculation methodology is introduced and the computational details are given in section 2. In section 3, the results of structural, optical, electric and thermal properties of ZnX binary compounds are presented and discussed. In this section we also compared our results with the already available experimental data and as well as theoretical calculations. Finally, the summary of the our main results and concluding remarks is given in section 4.

2. COMPUTATIONAL METHOD

The calculations of the structural, optical, electric and thermal properties are calculated in the frame work of Density Funtional Theory (DFT) [1]. To calculate these properties, we employed the full potential linearized augmented plane wave plus local orbitals (FP-LAPW + lo) as implemented in the Wien2k code [9-10]. We have used the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE) to explain the exchange and correlation effects [11]. ZnX compounds crystallize in the zinc-blende structure with space group F-43 m. The Zn atom is set at (0, 0, 0) whereas the X atom is set at (0.25, 0.25, 0.25). We have employed Murnaghan's equation of state [12] for the optimization of the total energy with respect to the unit cell volume.

Thus the equilibrium structural parameters have been calculated. The calculations were done with RMTkmax = 7, to achieve energy eigen value convergence. RMT is the smallest radius of the muffin-tin (MT) spheres and kmax is the maximum value of the wave vector. The respective values of muffin-tin radii (RMT) for Zn, S, Se and Te were taken to be 2.1, 2.0, 2.2 and 2.5 a.u. (atomic units) for all the calculations. The wave function has been expanded inside the atomic spheres with the maximum value of the angular momentum

lmax as 10. The irreducible Brillouin zone (BZ) of the zincblende structure has been decomposed into a matrix of $10 \times 10 \times 10$ Monkhorst–Pack k-points [13]. The iteration procedure is continued with total energy and charge convergence to 0.0001Ry and 0.001e, respectively

3. RESULTS & DISCUSSIONS 3.1. Structural and elastic properties

With the Murnaghan's equation of state [12], the variation of the total energy versus unit cell volume yields to the equilibrium lattice parameter (a_0) , bulk modulus B_0 , and the pressure derivative of the bulk modulus B₀'. The values of a0, B_0 and B_0' for the ZB structure of the binary ZnX at zero pressure are presented in Table 1. For ZnS, ZnSe and ZnTe, the energy minima take place for a0 = 5.371, 5.632 and 6.198 Å, which agree well with the experimental values of 5.412, 5.667 and 6.103 Å, respectively with the maximal error of 1.53% with respect to experimental values. It is obvious that well defined structural properties are helpful for further study of electronic and optical properties. The elastic constants of ZnX compounds with cubic structure have been determined using the method developed by Charpin incorporated in WIEN2k code [14]. By applying appropriate lattice distortions in a cubic lattice, three independent elastic constants C₁₁, C₁₂, and C444 are determined. The following three equations are considered for the calculation of the elastic constants.

$$B_0 = (C_{11}+2C_{12})/3$$
(1)

$$\Delta E_{\text{rhomb}} = ((C_{11}+2C_{12}+4C_{44})V_0\delta^2)/6$$
(2)

$$\Delta E_{\text{tetra}} = 6(C_{11}-C_{12})V_0\delta^2)$$
(3)

The first equation contains relation between the elastic constants (C_{11} and C_{12}) and the bulk modulus B0, obtained from Murnaghan's equation. Second equation is related to the variation of strain energy (ΔE_{rhomb}) versus volume-conserving rhombohedral strain (δ). Third equation is related to the variation of strain energy (ΔE_{tetra}) versus volume conserving tetragonal strain (δ). The calculated elastic constants for the zinc-blende ZnX are displayed in Table 2 with experimental result [15]. Calculated values are in a good agreement with available experimental data. The elastic constants decrease in magnitude with increase in lattice dimension from S to Te, due to cohesive energy decreases with the nearest-neighbour distance [16]. The mechanical stability in a cubic crystal requires the elastic constants satisfying the conditions as, C_{11} - $C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B_0 < C_{11}$. The elastic constants in Table 2 obey these conditions. Calculated values of three elastic constants namely C_{11}, C_{12} and C_{44} , are used to determine Bulk modulus, B₀, Young's modulus, Y , Isotropic shear modulus, G and Poisson ratio, ζ based on the following explicit expressions [17-18], $G = (G_V + G_R)/2$ (4)

Here, G_V is Voigt's shear modulus and G_R is Reuss's shear modulus for cubic crystals, expressed as:

$$G_{\rm V} = ((C_{11} - C_{12} + 3C_{44}))/5 \tag{5}$$

$$G_{R} = (5C_{44} (C_{11} - C_{12}))/(4C_{44} + 3(C_{11} - C_{12}))$$
(6)

The expressions for the Young's modulus and Poisson's ratio are given by

| Y = 9GB/(G+3B) | (7) |
|----------------------------|-----|
| $\sigma = (3B-2G)/(6B+2G)$ | (8) |

Table 3 displays the calculated values of elastic modulus. The bulk modulus B_0 represents the resistance to fracture while the

shear modulus G represents the resistance to plastic deformation. Ductility of the material can be characterised by B_0/G ratio [19]. The B_0/G ratio for all ZnX are greater than 1.75 (see Table 3) which reveals that the compounds are ductile in nature. The highest value of B_0/G ratio is 2.19 for ZnTe representing it most ductile among all the ZnX compounds. There is a correlation between the binding properties and ductility [20]. The bond character of cubic compounds is expressed in terms of their Cauchy pressure $(C_{12}-C_{44})$. With increase in positive Cauchy pressure, compound is likely to form metallic bond. Accordingly, the ductile nature of all ZnX compounds can be correlated to their positive Cauchy pressure having the metallic character in their bonds. As depicted in Table 3, the ZnTe has a highest positive Cauchy pressure resulting strong metallic bonding (ductility) in it as compared to other compounds. The calculated value of Young's modulus (Y) is shown in Table 3. It provides the degree of stiffness of the solid, i.e., the stiffer material has the larger value of Y and such materials have covalent bonds. Table 3 shows that the highest value of Y occurs for ZnS demonstrating to be more covalent in nature as compare to other ZnX compounds. Value of Poisson's ratio (ζ), as a measure of compressibility for ZnX compounds are between 0.29 and 0.30 which predict that all the compounds are compressible. Also the Poisson's ratios having values between 0.25 and 0.5 represent central force solids. In our case, the Poisson's ratios are around 0.3, which reveals that the interatomic forces in the ZnX compounds are central forces.

Table 1: Calculated lattice constant (in A°), bulk modulus B_0 (in GPa), pressure derivative B_0° for ZnX compounds compared to experimental works.

| | a_0 | B ₀ | B ₀ ' |
|---------------------------------|----------------|----------------|------------------|
| ZnS Present Expt. | 5.371 5.412 | 90.12 75 | 4.32 4.00 |
| ZnSe Present Expt. | 5.632 5.667 | 72.42 69.3 | 4.76 |
| ZnTe Present Expt. | 6.198 6.103 | 60.39 50.9 | 4.71 5.04 |

Table-2: Calculated values of elastic constants (C_{ij} in GPa) at equilibrium for ZnX compound.

| | C ₁₁ | C ₁₂ | C ₄₄ |
|---------------------------------|-----------------|-----------------|-----------------|
| ZnS Present Expt. | 111 104 | 71 65 | 69 46.2 |
| ZnSe Present Expt. | 91 85.9 | 63 50.6 | 59 40.6 |

| ZnTe | | | |
|---------|------|------|------|
| Present | 79 | 48 | 41 |
| Expt. | 71.7 | 40.7 | 31.2 |

Table – 3: Calculated values of elastic modulus (in GPa)

| | G | B0/G | C12- | Y | σ |
|------|----------|---------|-------|-------|-------|
| | (GPa) | | C44 | (GPa) | |
| | | | (GPa) | | |
| | | | | | |
| ZnS | 41.88662 | 2.15152 | 1.88 | 108.8 | 0.299 |
| | | | | | |
| ZnSe | 33.41409 | 2.16735 | 3.93 | 86.88 | 0.3 |
| | | | | | |
| ZnTe | 27.48057 | 2.19755 | 7.57 | 71.58 | 0.302 |
| | | | | | |

3.2. Electronic properties

The electronic band structure of Zn chalcogenides has been calculated. The calculated band structure for ZnX at equilibrium is shown in figure 1(a-c). The calculated band structure is in good agreement with other theoretical results [21-23]. The zero of the energy scale is set at the top of the valence band (VB). The energy band structures are calculated along the directions containing high symmetry points of the first Brillouin zone, namely $W \rightarrow L \rightarrow \Gamma \rightarrow X \rightarrow W \rightarrow K$. Each member of ZnX demonstrates the existence of the valence band maximum and conduction band minimum at the same symmetry point. This confirms the direct energy gap between the top of the valence band and the bottom of conduction band at \Box point. With the increase of the lattice parameters starting from the sulphide to the telluride, the X atom p bands shift up in energy as a common feature of II-VI compounds [24]. The calculated band gap is underestimated in comparison with experimental results, because of the simple form of GGA which cannot account the quasiparticle self-energy [25].

The zero of the energy scale is set at the top of the valence band (VB). The energy band structures are calculated along the directions containing high symmetry points of the first Brillouin zone, namely $W \rightarrow L \rightarrow \Gamma \rightarrow X \rightarrow W \rightarrow K$. Each member of ZnX demonstrates the existence of the valence band maximum and conduction band minimum at the same symmetry point. This confirms the direct energy gap between the top of the valence band and the bottom of conduction band at Γ point. With the increase of the lattice parameters starting from the sulphide to the telluride, the X atom p bands shift up in energy as a common feature of II–VI compounds.

The density of states (DOS) for ZnS is shown in figure 2(a-c). It is similar to that of ZnSe and ZnTe. The first structure in the total DOS is small and centered at around -12.29 eV, -12.37 eV and -11.18 eV for ZnS, ZnSe and ZnTe respectively. This structure arises from the chalcogen s states and it corresponds to the lowest lying band with the dispersion in the region around the r point in the Brillouin zone. The next structure appears at -6.20 eV, -6.56 eV and -7.09 eV for ZnS, ZnSe and ZnTe, respectively. It is an attribute of Zn d states with some p states of the chalcogen atoms and occupies largest number of states with flat bands clustered between -5.6 eV and -6.5 eV (for ZnS).



Figure 1a. Shows the Band Structure of ZnS



Figure 1b. Shows the Band Structure of ZnSe



Figure 1c. Shows the Band Structure of ZnTe



Figure 2a. Shows the Density of States of ZnS



Figure 2b. Shows the Density of States of ZnSe



Figure 2c. Shows the Density of States of ZnTe

Less dispersion of these bands results in sharp peaks. There is a wide spread in DOS in the energy range of -5.6 eV and zero energy for these compounds. The peaks in this energy interval arise from the chalcogen p states partially mixed with Zn s states and they contribute to the upper Valence Band. Above the Fermi level, the feature in the DOS originate mainly from the s and p states of Zn partially mixed with little of chalcogen d states. Band width of valence band as determined from the

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width of the peaks in DOS dispersion below Fermi level equal to 13.42 eV, 13.13 eV, 12.17 eV for ZnS, ZnSe and ZnTe, respectively. The results showing valence band width minimum for ZnTe, clearly indicate that the wave function for ZnTe is more localized than that for ZnS. This is in consistence with the fact that when the atomic number of the anion increases, a material becomes non-polar covalent with valence band states being more localized.

3.3. Optical properties

The dielectric function $\varepsilon(\omega)$ can describe the interaction of photons with electrons in the form of linear response of the system to electromagnetic radiation [26]. Dielectric function comprises of the imaginary part $\varepsilon_2(\omega)$ and the real part $\varepsilon_1(\omega)$. They are shown in figures 3 & 4. The absorption of ZnX binary compounds are shown in figure 5. Figures 6 and 7 represents the dielectric loss and the reflectivity of ZnO, ZnS, ZnSe and ZnTe. $L(\omega)$ describes the energy-loss of a fast electron traversing in the material [27]. Its highest peak gives rise to plasma frequency ωP . Generally it happens where $\varepsilon_2(\omega) < 1$ and $\varepsilon_1(\sigma)$ turns to the zero value [28]. The main peaks in the energy-loss spectra for different chalcogen atom (S, Se, and Te) are located at 12.78, 12.61 and 12.85 eV, respectively. Moreover, the main peaks of $L(\omega)$ start to decrease while the peaks in reflection spectra $R(\omega)$ start to increase. For example, the abrupt reduction of $L(\omega)$ occurs by 55% where the peak of $R(\omega)$ appears at 13.56eV. The reflectivity $R(\omega)$ of ZnX possesses small value approximately in the photon energy range from 0 to 3.1 eV. It demonstrates the transmitting nature of the material for the photon energy <3.1 eV. It is clear from the reflectivity spectrum that ZnS possesses more transmitting nature than ZnTe in the visible range.



Figure 3. Shows the Imaginary part (ϵ_2) of ZnX calculated based on DFT



Figure 4. Shows the Imaginary part (ϵ_1) of ZnX calculated based on ϵ_2



Figure 5. Shows the Absorption of ZnX



Figure 6. Shows the Dielectric Loss of ZnX



Figure 7. Shows the Reflectivity of ZnX

4. CONCLUSION

This paper reports a systematic study of the structural, electronic, elastic and optical properties of Zn-chalcogenides (ZnTe, ZnSe and ZnTe) have been studied with FP-LAPW + lo method in the framework of density functional theory. The quantities such as elastic constant, band structure, dielectric constants, dielectric loss and refractive index were obtained. The generalized gradient approximation (GGA) was considered for the exchange and correlation effects calculations. The results from FP-LAPW + lo method were found to be in better agreement with the experimental data in comparison to other calculation methods. The elastic constants maintain all conditions to be satisfied for mechanical stability of the compound. The profound ductility in ZnX compound was observed with the increase in chalcogen atomic number. The metallic character in their bonds is well demonstrated from the positive Cauchy pressure (C12-C44) values. The band structure of all Zn-chalcogenides confirms the direct energy gap between the top of the valence band and the bottom of conduction band at r point. In the linear optical response, the absorption threshold shifts toward lower energy with the increase in chalcogen atomic number. The strong interband transitions between the chalcogen outermost s state and Zn 3d states play the main role in the optical response.

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Growth, structural, mechanical and dielectric studies of undoped and urea doped L-alaninium maleate (LAM) crystals

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Abstract Undoped and urea doped L-alaninium maleate crystals were grown by solution method with slow evaporation technique. Solubility studies were carried out for the grown crystals and it is found that solubility increases with temperature for both the samples. XRD studies were performed to find the crystal structure of the samples. NLO activity of the grown crystals was studied using a Nd:YAG laser and SHG efficiency was found for both the samples. Microhardness studies were performed to understand the mechanical strength of the samples. Measurements of values of dielectric constant and dielectric loss were carried out and the electrical processes that are taking place in the samples are discussed.

Keywords: Amino acid complex; NLO; doping; single crystal; solution growth; spectroscopy; SHG; hardness

1. INTRODUCTION

Nonlinear Optical (NLO) materials have potential applications in Second Harmonic Generation (SHG), optical storage, optical communication, photonics, .electro-optic modulation, optical parametric amplifiers , optical image processing etc [1,2]. L-alanine is an alpha amino acid with NLO activity and it has the chemical formula CH₃CHNH₂COOH. It is a white odorless crystal powder and easily dissolves in water, slightly dissolves in alcohol and undissolves in ether. L-alanine is a conditionally essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system. L-alanine strengthens the immune system by producing antibodies, helps in the metabolism of organic acids and sugars and is used by protein synthesis and immune system regulation [3,4]. Considering the importance of L-alanine, it is combined with maleic acid to form L-alaninium maleate (LAM). To improve the NLO activity and other properties of LAM crystal, urea was added as the dopant into LAM in this work. The aim of this work is to report on the growth of undoped and urea doped LAM crystals and to discuss the results obtained from various studies such as solubility studies, XRD, hardness studies, SHG studies and dielectric studies.

2. GROWTH AND SOLUBILITY

L-alaninium maleate (LAM) sample was prepared from aqueous solutions of AR grade L-alanine and maleic acid taken in 1:1 molar ratio. The evaporation of the solution yielded LAM crystals. To obtain urea doped LAM, 1 mole% of urea was added the solution of LAM. The key factor for successful growth of any crystal is the proper selection of solvents. To find out the suitable solvent, the solubility test was carried out by gravimetrical method [5] and here water was found to be the suitable solvent for growing crystals. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined. The solubility curves for undoped and urea doped LAM samples were plotted and they are shown in figure 1. It is observed that solubility increases with temperature for both the samples. When urea was doped into LAM crystal, it is noticed that the solubility increases leading to dissolution of more solute in the same amount of solvent.



Figuere 1. Solubility curves for undoped and urea doped LAM samples.

3. CHARACTERIZATION OF THE GROWN CRYSTALS

Single crystal XRD data of undoped and urea doped LAM crystals were collected from a single crystal X-ray diffractometer with graphite mono chromated MoK_a

radiation. The obtained crystallographic data for undoped LAM and urea doped LAM crystals are a=5.572(2) Å, b = 7.415(4) Å, c = 23.674(3) Å, $\alpha = \beta = \gamma = 90^{\circ}$ and a= 5.598(4) Å, b=7.465(1) Å, c= 23.592 (2) Å, $\Box = 90^{\circ}$, $\Box = 90^{\circ}$ $\Box = 90^{\circ}$ respectively. From the data, it is observed that both the grown crystals crystallize in orthorhombic crystal systems. The number of molecules per unit cell (Z) for both crystals of this work is found to be 4. The slight changes in the lattice parameters are due to incorporation of urea in the lattice of LAM crystal.

The mechanical property of crystals can be analyzed by carrying out microhardness studies using a Leitz Vickers microhardness tester. Measuring microhardness gives an idea about the mechanical strength of a material. The hardness of a material is a measure of its resistance to plastic deformation. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect (ISE). The hardness number was measured for undoped and urea doped LAM crystals by applying different loads. The Vickers microhardness number was calculated using the relation $H_v = 1.8544 \text{ P/d} \text{ kg/mm}^2$ where P is the applied load and d is the diagonal length of the indentation impression. The variations of Vickers hardness number with the applied load for both the samples are presented in the figure 2.



Figure 2. Variation of hardness number with the applied load for undoped and urea doped LAM crystals.

It is observed from the figure that the hardness increases as the load increases. Cracks are formed beyond 100 g and the formation of cracks on the surface of the crystal beyond the load 100 g is due to the release of the internal stresses generated locally by indentation. The increase of microhardness with increasing load is in agreement with the Reverse Indentation Size Effect (RISE) as reported in the literature [6].

Second Harmonic Generation (SHG) test for the grown pure and urea-doped LAM crystals was performed by the powder technique of Kurtz and Perry [7] using a pulsed Nd:YAG laser(Model: YG501C, \Box =1064 nm). Pulse energy

of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 300-500 μ m and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Mirocrystalline material of potassium dihydrogen phosphate (KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using an optical cable attached to a fluorescence spectroscope(Model: DID A-512 G/R). The SHG efficiency for undoped LAM crystal is found to be 1.15 times and for urea doped LAM crystal is observed to be 1.34 times that of KDP sample and hence the samples are the second harmonic generators.

The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown. When an electric field acts on any matter the latter dissipates a certain quantity of electrical energy that transforms into heat energy. This phenomenon is commonly known as loss of power, meaning an average electric power dissipated in matter during a certain interval of time. The amount of power losses in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses. The lower the dielectric loss the more effective is a dielectric material. Dielectric constant and dielectric loss values of crystalline samples were measured using a two-probe arrangement and an LCR meter. The measured values of dielectric constant and dielectric loss at different temperatures at frequency of 10³ Hz for the samples viz. undoped and urea doped LAM crystals are presented in the figures 3 and 4.



Figure 3. Variation of dielectric constant with the temperature at frequency of 1000 Hz for undoped and urea doped LAM crystals.

From the results, it is observed that dielectric parameters such as dielectric constant and loss factor increase with increase in temperature for both the samples. The same behaviour is exhibited by dielectric loss (tan \Box). In accordance with Miller's rule, the low value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient and low values of dielectric loss reveals the high optical quality of the crystals with lesser defects, which is the desirable property for NLO applications [8]. Variation of the dielectric parameters of the sample with temperature is
generally attributed to the crystal expansion, the electronic, space charge and ionic polarizations and also due to the thermally generated charge carriers. When urea is added into the LAM crystal as the dopant, it is noticed that the dielectric parameters are found to be increasing which may be due to presence of defects in the host crystal.



Figure 4. Variation of dielectric loss with the temperature at frequency of 1000 Hz for undoped and urea doped LAM crystals

4. CONCLUSION

Two samples viz. undoped and urea doped L-alanine maleate crystals were grown by solution method. Solubility in water is found to be increasing with temperature for the both samples. XRD study reveals that the grown crystals crystallize orthorhombic structure. The mechanical strength of the samples was analyzed by hardness studies and SHG was tested by Kurtz powder method. The dielectric constant, loss factor and SHG values reveal that the grown crystals are suitable materials for optical communication, electro-optic modulation and optical computing.

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Design and Development of Polyaniline-coated Fabric Strain Sensor for Goniometry Applications

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Abstract: In the last few years, the smart textile area has become increasingly widespread, leading to developments in new wearable sensing systems. As conventional sensor techniques often cause problems for long term patient monitoring (e.g. skin irritation, hampering wires), elegant solutions are explored to integrate sensors in clothing. By using the textile material itself as a sensor, the integration is increased resulting in even more patient friendliness.

In this paper, a flexible fabric strain sensor with high sensitivity, good stability and large deformation is reported. It is fabricated by in-situ polymerization of polyaniline on the fabric substrate at low temperature. Thickness and morphology of the conducting thin film on the surface of the fibers were examined by scanning electron microscopy (SEM). The resistivity of the PANi coated fabric was measured using standard two probe apparatus.

The measurement of the conductivity change with strain shows that the fabrics so prepared exhibits a high strain sensitivity while its good stability is indicated by a small loss of conductivity after the thermal and humidity aging tests, and supported by the slight change in conductivity over storage of 90 days. The developed flexible strain sensor can be used in the preparation of smart garment for goniometry applications.

Keywords: conductivity, goniometry, fabric strain sensor, polyaniline, sensitivity

1. INTRODUCTION

Inherently conducting polymers such as polypyrrole and polyaniline are often referred to as a "synthetic metals", which possesses the electrical and magnetic properties of a metal, while retaining the mechanical properties of a polymer. Active research has been carried out to investigate the application of these materials in corrosion protection, rechargeable batteries, electrochromic displays, conducting composite materials, biosensors, chemical gas sensors, actuators, microextraction platforms, electronics, electrochemical energy sources, optical devices and smart fabrics.

Electro-textiles can be defined as textiles with unobtrusively built-in electronic and photonic functions. They are mostly used for electromagnetic shielding, anti-static and heating purposes, and also for soft circuits: electric circuits or sensors made out of a combination of special fabrics, threads, yarns and electronic components. Electrical functions can be embedded in textiles by using weaving, knitting and embroidery or nonwoven production techniques. The integration of electronic properties directly into the clothing environment carries some advantages such as increased comfort, mobility, usability and aesthetic properties. However, there are some challenges to be addressed. Yarns that are used for making cloth should be fine and elastic in order to ensure the wearer's comfort. The fibres have to be able to withstand handling and fabrics should have low mechanical resistance to bending and shearing which means they can be easily deformed and draped.

The creation of textile-based strain sensors has attracted researchers' attention so many investigators have

studied this area and numerous different kinds of technique have been used in order to create strain sensing structures. These sensors have been used to measure human body movements or respiratory activity [1&2]. De Rossi et al. [3] created strain sensing fabrics by coating Lycra/cotton fabrics with polypyrrole and carbon loaded rubbers. Polypyrrole-coated fabrics showed an average gauge factor of about -13. These strain sensing fabrics exhibited a strong variation of strain-resistance with time and they showed a high response time to applied mechanical stimulus. Fabrics coated with carbon loaded rubber had a gauge factor of approximately 2.5 and fabric sensors made with this type of material showed good strain sensing properties between 1% and 13% strain. Xue et al. [4] also created strain sensing structures by coating nylon 6 and polyurethane fibres with polypyrrole. According to this research, polypyrrole-coated nylon 6 fibres showed good sensing performance, whereas polypyrrole-coated polyurethane fibres did not produce promising results as a strain sensing structure. Also, Mattmann et al. [5] created a strain sensor by using a thermoplastic elastomer and carbon particles and they were able to recognize upper body postures with an accuracy of 97%.

We report a PANi coated flexible strain sensor which was prepared by in-situ polymerization of polyaniline on the fabric substrate at low temperature. The sensor so prepared fabricated shows both high strain resistivity for a large deformation and a good environmental stability.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Aniline, concentrated HCl, and Ammoniumpersulfate (APS), all of AR grade and obtained from S.D. Fine Chemicals Ltd., India, were used. Aniline was distilled twice before use. 92% nylon and 8% lycra single jersey fabric was used. The fabric specifications are, Thickness: 0.573 mm, GSM: 200grams, wales per inch (WPI): 64, course per inch(CPI): 88.

2.2 Synthesis of conductive fabrics

Conductive fabrics were developed by in situ chemical polymerization of aniline on the fabrics. In this process, freshly distilled 0.5 M aniline was dissolved in the bath containing 0.35N HCL solution for diffusion. A vigorous stirring was given to the bath containing mixtures of aniline and aqueous acid to attain the homogeneous mixing. Dry preweighed fabric sample was placed in the above solution at 40°C and allowed for 2 h to soak well with the monomer and dopant solution. 0.25M ammonium per sulfate was separately dissolved in 0.35N HCL solution for polymerization. The aqueous oxidizing agent in the separate bath was then slowly added in to the diffusion bath to initiate the polymerization reaction. The oxidant to aniline ratio was kept at around 1.25. The whole polymerization reaction was carried out at 5°C for 1hour. After completing the polymerization process, the coated fabric was taken out and washed in distilled water containing 0.35N HCL and dried at 60 °C [6]. The SEM images were recorded by JEOL SEM (model JSM- 6360) to study the surface morphology of the control and polyaniline treated samples in the longitudinal view.

2.3 Electrical resistance measurements

Electrical resistance measurements were performed on all samples after conditioning the samples in a standard atmosphere. The resistance was measured ten times on each side of the sample and the average values were taken. The American Association of Textile Chemists and Colourists (AATCC) test method 76-1995 was used to measure the resistance of the samples and the surface resistivity of the fabric was calculated as follows

 $R = R_s(l/w)$

where *R* is the resistance in ohms; R_s , the sheet resistance or surface resistivity in ohms/square; *l*, the distance between the electrodes; and w, the width of each electrode

2.4 Test Procedure for Knitted Strain Sensors

The PANi coated conductive nylon lycra fabric having size of $150 \text{mm} \times 30 \text{mm}$ was extended with help of fabric extension meter from an initial length of 15cm and then they were extended for 50 % i.e. 8 cm at intervals of 1 cm. The resistance change thus caused due to the extension was measured using Waynekerr 4321 LCR Meter. The extension level of 50% was chosen to mirror typical human body extensions, as the proposed sensor can be used for monitoring human body movements. The sample was measured five times and the relaxation between measurements was 10 sec.

In strain sensors, the gauge factor (GF) is an important parameter and it gives information about the sensitivity of the sensor. The GF is calculated as follows:

$$GF = \Delta \mathbf{R}$$
(1)
$$\varepsilon \mathbf{R}$$

Where:

 ΔR = the change in the resistance;

R = the initial resistance (the resistance before extension);

 ε = the strain value.

2.5 Experimental set up for Joint Angle Measurement

The PANi coated conductive nylon lycra fabric having size of 150 mm \times 30 mm was attached to an elbow sleeve using a Velcro as shown in Figure 1a. The sleeve which is integrated with sensors was fixed in a subject arm as shown in Figure 1b for the measurement of resistance change for angular displacement. The arm was moved for different angle positions with use of a mechanical goniometer and corresponding resistance change was noted using Waynekerr 4321 LCR Meter. Three trials were taken and corresponding readings has been recorded. Then, the angles were converted into equivalent resistance and calibration done. Hence, the resistance change can be measured for further use and can be converted into angles based on the calibration [7].

2.6 Aging behavior Measurement

Both thermal and humidity aging tests were carried out by recording the conductivity change of the PANi-coated fabric put in a Programmable Environmental Test Chamber (Remi Instrument Ltd, Mumbai), where both the temperature and humidity can be controlled. For the thermal aging, the humidity is always kept at 65%RH. The temperatures investigated include 20, 35, 50 and 60° C and the temperature changes every two hours. The humidity aging was carried out at 30° C. The humidities investigated include 40, 55, 70 and 90% RH and the humidity changes every two hours [8].

3. RESULTS AND DISCUSSION3.1 SEM Studies

The surface views of SEM micrographs of the control nylon lycra fabric and nylon lycra + PANI are shown in Figure 2. Just a glance at the fabric with the naked eye shows a uniform color (in this case, green), indicating that PANi has penetrated into the fabric. However, the SEM studies reveal how evenly the surface has been coated as well as the depth of penetration.

From the SEM studies, it is clear that the PANi particles are very evenly deposited on the fabric, and are seen as small globules. The surface studies clearly reveal uniform distribution even at the microscopic level, which is necessary for the reproducibility and reliability of applications. The



Figure 1 a) Sensor Integrated Elbow Sleeve b) Elbow angle measurement using developed sensor

diffusion and polymerization of aniline in the fabric is evident at the macroscopic level in terms of the increased thickness of the fabric, from 0.573 mm to 0.575mm. The fibres are swelled due to polyaniline impregnation. Because of this swelling of fibres, the thickness of PANI coated fabrics increases.

3.2 Electrical properties

Surface resistivity is a material property that is normally considered constant and ideally independent of measurement technique. Surface resistivity measurement is often used to characterize fabric resistivity and is typically reported as ohm/square. We studied the electrical resistivity of the polyaniline coated fabric by two probe resistivity measurement in a normal environment at 65% RH. The surface resistivity value of the fabrics coated with polyaniline is 3.5 K ohm/square.

3.3 Electrical resistivity for linear extension

The PANi coated nylon lycra fabric sample was extended up to 50% extension and the changes in resistance with extension were noted and are as shown in the Table 1 and Figure 3. The fabric sensor has negative resistance versus elongation change effect, which means that the resistance decreases with extension. The reason for that is the





Figure 2 a) control nylon lycra fabric b) PANi treated nylon lycra fabric

construction of the sensor. When the sample is stretched, the course and wale spacing decreases, higher contact pressure occurs between adjacent course and wales. The conductive connections increase and the resistance decreases. The developed fabric strain sensor has the average gauge factor of 0.92.

According to Holm's contact theory:

$$Rc = \frac{\rho}{2} \sqrt{\pi . H / nP} \qquad (2)$$

Where:

Rc = contact resistance; ρ = electrical resistivity; H = material hardness; n = number of contact points;

P = contact pressure.

| Length | Tri | al 1 | Tri | al 2 | Tri | al 3 | Tri | al 4 | Tri | al 5 |
|--------|-----------|----------|-----------|---------------------|-----------|----------|--------------------|----------|-----------|----------|
| in cm | Extension | Recovery | Extension | Recovery | Extension | Recovery | Extension | Recovery | Extension | Recovery |
| 15 | 22.31 | 24.124 | 24.088 | 24.836 | 24.038 | 24.87 | 22.97 | 25.161 | 23.455 | 25.068 |
| 16 | 21.146 | 22.044 | 21.302 | 23.557 | 21.519 | 22.67 | 21.239 | 22.758 | 21.575 | 23.023 |
| 17 | 19.457 | 20.844 | 20.352 | 22.438 | 19.801 | 20.827 | 19.702 | 21.234 | 20.017 | 21.822 |
| 18 | 18.434 | 19.285 | 19.055 | 20.045 | 18.759 | 19.639 | 18.53 | 19.937 | 18.902 | 20.367 |
| 19 | 17.585 | 18.67 | 17.953 | 19.732 | 17.633 | 18.92 | 17.642 | 19.084 | 18.299 | 19.693 |
| 20 | 16.74 | 17.767 | 17.018 | <mark>18.497</mark> | 17.082 | 17.95 | 17.175 | 18.258 | 17.584 | 18.748 |
| 21 | 16.215 | 17.022 | 16.612 | 17.649 | 16.576 | 17.333 | 16.787 | 17.475 | 16.912 | 17.879 |
| 22 | 15.71 | 16.156 | 16.12 | 16.628 | 16.157 | 16.469 | 16.194 | 16.717 | 16.459 | 16.913 |
| 23 | 15.34 | 15.34 | 15.705 | 15.705 | 15.517 | 15.517 | <mark>15.57</mark> | 15.57 | 15.925 | 15.925 |
| GF | 0.0 | 371 | 0.7 | 798 | 1. | 065 | 0.9 | 925 | 0.9 | 941 |

Table 1: Electrical resistance changes in ohm with the elongation of PANi coated fabrics

From equation (2), it can be see that the electrical resistivity and material hardness are constant for a given material, but the number of contact points and the contact pressure are variable depending on the sensor design. Thus, higher contact pressure and increased number of contact points between conductive parts lower the contact resistance [9&10].



Figure 3 : Electrical resistance changes in K ohms with the elongation of PANi coated fabrics



Figure 4 Change in resistance in Kohms with angular displacement

3.4 Measurement of resistance with varying angles

The change in resistance for various angles of movement of elbow is shown in Table 2 and Figure 4. The samples tend to have a good repeatability property for angle - resistance change. There was a steady decrease in resistance with up to 90° flexion of the elbow after that the change in resistance is not significant.

| Table 2 Electrical | resistance | changes | in 1 | K | ohms | with |
|--------------------|------------|----------|------|----|------|------|
| angular displaceme | nt of PANi | coated f | abri | cs | | |

| Angl | Trial 1 | | Tri | Trial 2 | | Trial 3 | |
|------|---------|---------|--------|---------|--------|---------|--|
| C | Bendin | Recover | Bendin | Recover | Bendin | Recover | |
| | g | у | g | у | g | у | |
| 0 | 38.636 | 39.932 | 39.884 | 40.929 | 40.26 | 41.235 | |
| 10 | 41.11 | 39.658 | 43.167 | 40.65 | 42.195 | 43.466 | |
| 20 | 42.412 | 38.487 | 39.43 | 36.571 | 43.144 | 42.074 | |
| 30 | 39.347 | 36.894 | 36.337 | 35.548 | 41.449 | 41.94 | |
| 40 | 36.494 | 35.288 | 34.765 | 34.477 | 38.318 | 39.319 | |
| 50 | 34.781 | 34.485 | 33.781 | 33.67 | 36.039 | 37.749 | |
| 60 | 32.968 | 33.534 | 32.394 | 32.21 | 34.66 | 36.199 | |
| 70 | 32.345 | 32.579 | 31.213 | 31.651 | 33.331 | 34.055 | |
| 80 | 31.832 | 32.052 | 30.607 | 31.106 | 32.463 | 33.164 | |
| 90 | 31.073 | 31.073 | 30.288 | 30.288 | 31.345 | 31.345 | |

3.5 Aging behavior

In addition to high sensitivity, good environmental stability is especially important for the practical application. The conductivity degradation of PANi is closely related to its reaction with oxygen, especially under elevated temperatures, and moisture. Therefore, the stability of the PANi coated nylon lycra fabric was first investigated by the thermal aging and humidity aging tests. The thermal aging test is conducted by changing temperature from 20 to 60° C, and the conductivity change with temperature of the PANi coated nylon lycra fabric during the thermal aging process is presented in Table. 3. It can be seen that the difference in resistance between the temperatures is quite small. In addition, at low temperature only a slight increase in resistance is observed which may be related to the stability of the dopant ion and the re arrangement of the PANi chain. Humidity can also exert an influence on the conductivity of PANi. The conductivity change with humidity of the sensor is presented in Table. 4. It was found that the humidity increase can only slightly decrease the resistance of the sensor.

| Table 3 Resistance | change with | n Temperature |
|--------------------|-------------|---------------|
|--------------------|-------------|---------------|

| Temperature in ^o C | Surface Resistance in Kohm/square |
|-------------------------------|--------------------------------------|
| 20 | 3.8 |
| 35 | 3.5 |
| 50 | 3.2 |
| 60 | 3.0 |

 Table 4 Resistance change with RH%

| Relative Humidity in % | Surface Resistance in Kohm/square |
|------------------------|--------------------------------------|
| 40 | 3.7 |
| 55 | 3.5 |
| 70 | 3.3 |
| 90 | 3.2 |

The thermal and humidity aging tests show that the conductivity of the strain sensor from PANi -coated fabric is only slightly dependent on the humidity and temperature. Therefore, it can be concluded that the effect of the temperature and humidity on the conductivity of the strain sensor can be ignored. A more direct proof of the stability of the PANi -coated fabrics is the variation of the conductivity and sensing properties of the sensor during storage of a long time. We found that the surface resistivity of the PANi coated fabric increases from 3.5 K ohm/ square to 5 K ohm/ square after 90 days. Therefore, it can be concluded that the flexible strain sensor from PANi coated fabrics shows good environmental stability.

4. CONCLUSIONS

In summary, a polyaniline-coated fabric strain

sensor featured with high strain sensitivity, good stability and large deformation has been developed. The sample was tested for change in resistance with linear extension and observed that the developed fabric strain sensor has a good gauge factor value of 0.92, which is a good sensitivity value. The developed fabric strain sensor was attached to an Elbow sleeve for joint angle measurement and it was found that up to 90° joint movement can be measured with repeatability. The PANi-coated fabric strain sensor so prepared is expected to find applications in sensing garment, wearable hardware and rehabilitation, etc.

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Alkali P-Nitrophenolates for Short Wavelength Laser Generation

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Abstract: Single crystals of alkali p-Nitrophenolates namely sodium p-nitrophenolate dihydrate (SPNP), potassium p- nitrophenolate trihydrate (LPNP) using Group I elements (Na, K, Li) and p-nitrophenols were grown by solvent evaporation method. Single crystal XRD analysis shows that SPNP and LPNP crystallize in noncentrosymmetric space group while PPNP is centrosymmetric. Using Autox software, all the peaks in the recorded powder XRD spectrum of the samples were identified and indexed. The FT – IR spectra of the sample reveals the characteristic vibrations of the functional groups present in alkalinitrophenolates. A weak absorption band around the region $1589-1641 \text{ cm}^{-1}$ confirms the presence of the phenolic ring. A broad intermolecular hydrogen bonded OH stretching at 3325 cm^{-1} of p- nitrophenol is shifted which shows the increase in the polarizable nature of p-nitrophenol and thus easily forms a metal (sodium/ potassium/ lithium) coordination compound. UV-Vis spectrum shows that all the crystals are transparent above 400 nm and has a wide optical window in the visible region. Intense absorption peak in the UV region may be due to the colored nature of the compound. Addition of metal ion (sodium/potassium) modifies the optical transparency of the original molecule (p-nitro phenol) and consequently introduces a bath chromic shift of 90/40 nm in the crystal transparency of the samples. Kurtz powder technique result shows that the relative SHG efficiency of SPNP and LPNP was nearly 5 and 9.25 times of KDP.

Key Words: p-Nitrophenol, SHG Efficiency, Alkali Metals.

1. INTRODUCTION

The p-nitrophenolate derivatives are the other forms of metalorganic coordination complexes. The prototype organic NLO material contains one or more delocalized bonds, typically a ring structure like benzene. When substituted with donor and acceptor at the para position, the bonds get aligned and thus have a large induced dipole moment under the influence of electromagnetic fields. p-nitrophenol is a typical example for the above strategy [1]. It has often been found that such structures, when packed as crystals tend to be centrosymmetric, thus leading to macroscopically vanishing dipole moment. However, when it reacts with the bases, the resulting compound is acidic with a non-vanishing dipole moment for the donor-acceptor π conjugate systems [2, 3]. The life time of an optical device (electro- optic modulators, parametric oscillator, etc.) is strongly dependent on mechanical and thermal properties of the nonlinear material. Organic materials are more fragile than inorganics owing to van der Waals bonds which maintain the cohesion of molecular packing. Based on these favorable properties, three nitrophenolates namely (i) sodium p-nitrophenolate dihydrate (SPNP), (ii) potassium p- nitrophenolate monohydrate (PPNP) and (iii) lithium p-nitrophenolate trihydrate (LPNP) have been synthesized and their optical properties were thoroughly investigated and reported.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis and Crystal Growth

The basic chemical reaction considered for synthesis is that a caustic alkali base (alkali hydroxide) will lose a proton in a

weak acidic (p- nitrophenol) leading to the formation of the salt. Thus in the present investigation, the salt is obtained by dissolving p-nitrophenol in alkali hydroxide (NaOH, KOH, LiOH) solution at 32°C in the molar ratio 1:1:30 for p-nitrophenol, alkali hydroxide and double distilled water respectively. By cooling the solution to room temperature a yellow crystalline powder is obtained.

From solubility studies, methanol was found to be the best solvent to grow SPNP and PPNP, while water was chosen for LPNP. Then the prepared solutions were allowed to slow evaporation, after a period of seven days yellow coloured single crystals of SPNP, PPNP and LPNP were obtained.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

The grown crystals were subjected to single crystal X-ray diffraction using a Enraf Nonius CAD-4 single crystal X-ray diffractometer with Cu K α radiation ($\lambda = 1.54060$ Å) to determine the unit cell dimensions. XRD analysis shows that SPNP crystal belongs to the orthorhombic system with a

noncentrsymmetric space group Ima2. The PPNP belongs to monoclinic system with a centrosymmetic space group P2₁ /c, which does not exhibit second order NLO activity. Also LPNP crystallizes in monoclinic system with a noncentrsymmetric space group Pa. Their cell dimensions are given in the Table 1. All the unit cells have (Z = 4) tetra molecules and have a suppressed growth along c axis.

It is interesting to note that elements in the complexes that are more electronegative induce more delocalization of electrons, favoring the noncentrosymmetric structure [4].

This is the reason why, PPNP is centrosymmetric while LPNP and SPNP are noncentrosymmetric as the electro negativity of alkali metals Li (0.98), Na (0.93) and K (0.82) falls down as one move down the Group.

Table 1. Cell Parameters of Nitrophenolates

| Sampl e | a (Å) | b (Å) | c (Å) | β (deg) | V (Å ³) |
|------------|---------------|---------------|---------------|------------|---------------------|
| SPNP | 6.896 (7) | 19.709 (6) | 6.443 (3) | 90 | 875.68 (9) |
| PPNP | 10.561 (3) | 7.379 (2) | 11.299 (4) | 117.8 0 | 778.72 (3) |
| LPNP | 10.838 (8) | 7.519 (4) | 11.31 (4) | 90.54 | 925.7(9) |

The powder samples were subjected to powder XRD (Figure 1) analysis using a X'Pert diffractometer with CuK α radiation (λ =1.5418 Å). The computer program AUTOX was used to index all the observed reflection in the XRD pattern and to calculate the corresponding lattice parameters. The lattice parameter evaluated from PXRD agrees very well with single crystal XRD data.

The figure 1C explains the comparision of particle size, lattice constant variation with the calcination temperature. In is observed from the figure that, particle size increases with increasing calcination temperatures and lattice constant decreases with temperatures.

3.2 Molecular Characterization

The FT – IR spectra of SPNP, PPNP and LPNP reveals that the characteristic vibrations of the functional groups present in nitrophenolates.



Figure 1 Powder XRD Pattern of Nitrophenolates.

The absorptions in the lower frequency region $(400 - 500 \text{ cm}^{-1})$ are due to the overtones of the fundamental vibrations of p-nitrophenolates. The vibrational frequencies of the functional groups present in alkali p-nitrophenolates are compared with the p- nitrophenol (PNP) in Table 2

Table 2. FT-IR bands of alkali p-nitrophenolates.

| | Wavenumber (cm ⁻¹) | | | | |
|------|--------------------------------|------|--------|-----------------------------|--|
| PNP | LPNP | SPNP | PPNP | Assignment | |
| 3325 | 3408 | 3189 | 3211 | v_{s} (OH) | |
| 3060 | 3059 | Ι | 3045 * | ν _s (C-H) | |
| 1613 | 1666 | 1682 | 1665 | δ (О-Н) | |
| 1590 | 1573 | 1576 | 1601 | v_{s} (NO ₂) | |
| 1494 | 1495 | 1484 | 1467 | ν _s (C=C) | |
| 1326 | 1320 | 1302 | 1343 | v_{as} (NO ₂) | |
| 865 | 855 | 853 | 846 | $v_{as} (C=C)$ | |
| 817 | 822 | 814 | 757 | δ (C-H) | |
| 710 | 705 | 703 | 699 | δ (C=C) | |
| 642 | 647 | 644 | 629* | δ (O-H) | |
| _ | 497 | 494 | 483 | (Li/ Na/ K) | |

 v_{s-} symmetric stretching

 v_{as} – asymmetric stretching δ - bending

A weak absorption band around the region $1589 - 1641 \text{ cm}^{-1}$ confirms the presence of the phenolic ring. The shift in broad intermolecular hydrogen bonded OH stretching at 3325 cm⁻¹ increase the polarizable nature of p-nitrophenol to a higher order and it easily forms a metal coordination compound and hence confirms the molecular structure of the synthesized compounds.

3.3 Linear Optical Characterization

Optical transmittance of the crystalline samples was recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the UV – Vis region. In SPNP single crystals, 60% optical transmittance occurs at 520 nm and it has a good optical transmittance window in the region 520-1500 nm. In PPNP, the intramolecular charge transfer between the donor and acceptor groups give an intense absorption band (EtOH as solvent) in the UV region with λ_{max} at 388 nm and 310nm. This may be due to the colored compound absorbing in the visible region. In LPNP, 80 % transparency occurs at 450 nm and is almost transparent till 1500 nm (Figure 2). Addition of metal ion (sodium/potassium/lithium) modifies the optical transparency of the original molecule (p-nitro phenol) and consequently introduces a bath chromic shift of 90/40 nm in the crystal transparency.



Figure. 2 Optical Transmittance of Nitrophenolates

3.4 Non-linear Optical Characterization

The synthesized salts of p-nitrophenolates were imposed for SHG test by Kurtz powder technique using a Q-switched Nd:YAG laser (1064 nm, 10 ns, 10 Hz). The test reveals that SPNP, LPNP exhibits SHG and no SHG signal was observed for PPNP. In SPNP and LPNP, metal atom is ionically bonded with p-nitrophenol introducing the noncentrosymmetry, which is an essential criterion for SHG. The results are compared with the pulverized KDP and the relative powder SHG efficiency was found to be 5 and 9.25 times greater than KDP for SPNP and LPNP respectively.

It is worthwhile to note that a material with smaller ionic radii has larger polarizability and hence larger nonlinear polarization[4]. Thus LPNP with lowest ionic radii alkali (Li = 0.76 Å) metal has higher SHG efficiency than other alkali



Figure. 3 Particle size vs. SHG output.

nitrophenolates. The intensity of the SHG output as a function of particle size was measured. The SHG output of SPNP increases with respect to the range of particle sizes, indicating the phase matchable character of the SPNP. While for LPNP, SHG output decreases with increase in particle size, showing the non-phase matchable nature of LPNP (Figure 3).

4. CONCLUSION

In the present investigation, attempts were made to synthesize certain semiorganic NLO materials based on nitrophenolates by acid-base reaction using alkali metals. Single crystals of considerable sizes were grown following the low temperature solution growth technique. X-ray diffraction studies reveal that SPNP and LPNP crystallize in the noncentrosymmetric space group with prominent crystallographic planes suitable for further studies. All the crystals exhibit a wide optical transmittance window (450 - 1500 nm) in the UV-Vis region irrespective of the substitutions. From the powder SHG efficiency studies the phase matchable SPNP and non phase matchable LPNP with high SHG efficiency (nearly 5 and 9.25 times of KDP) are found to be the potential candidates for the generation of short wavelength lasers by frequency doubling phenomena.

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Growth and Characterization of Manganese (II) Sulphate and L-Lysine doped Manganese (II) Sulphate (LMnSO₄) Crystals

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Abstract: Single crystals of Manganese (II)sulphate doped with basic amino acid L-Lysine were grown successfully by slow evaporation method at ambient temperature. The concentration of dopants in the mother solution was varied from 1gm to 2gm. The solubility data for all dopant concentration were determined. The semiorganic material LMnSO₄ was synthesized and its structure was confirmed by powder X-ray diffraction study. Fourier transform infrared spectroscopy study confirms the incorporation of L-Lysine into MnSO₄ crystal. The doped crystals are optically better and more transparent than the pure ones having wide transmission spectra lying between 190 and 1100 nm. The dopant increases the hardness value of the material and it also depends on the concentration of the dopant. The dielectric loss of the material was calculated using dieletric measurement.

Keywords: Crystal morphology; X-ray diffraction; Growth from solutions; Manganese compounds;

1. INTRODUCTION

People grow crystals for two main reasons, to understand how crystals grow (aesthetic) and for the utility (scientific or technological applications of the grown crystals); for either of these, one must evaluate the quality of the crystals grown. The responsibility for the exquisiteness of the crystal is due to their structural simplicity, symmetry and purity. In recent years several studies deal with organic, inorganic and semiorganic molecules and materials due to the increasing need for cheap and easily processable materials for photonics applications. Semi organic crystals have the combined properties of both inorganic and organic crystals like high damage threshold, wide transparency range, less deliquescence and high non-linear co-efficients which makes them suitable for device fabrication ¹. In order to improve chemical stability, efforts have been made on amino acid with organic and inorganic compounds due to laser damage theroshold, and nonlinear and linear optical properties. Due to its properties and various applications in Bio-medical areas,L-Lysine was selected for the present work. Among the many functions of the amino acids, L-Lysine is capable to form collagen and repair tissues in the body. Like many metal sulphates, manganese (II) sulphate forms a variety of hydrates; monohydrate, pentahydrate and heptahydrate. The monohydrate is most common. In this present work, Manganese(II)sulphate and L-Lysine doped Manganese(II)sulphate crystals were synthesized and characterized by X-ray diffraction (XRD), Fourier Transform Infrared(FTIR), UV-Visible Dielectric study, and Microhardness techniques.

2. MATERIALS AND METHODS

The 100 ml of distilled water was measured and

taken in a cleaned beaker. 10g of Manganese (II) Sulphate (MnSO₄) Merck company-AR Grade was weighed and added with distilled water. The solution was allowed to stir using Magnetic stirrer. After 5 minutes MnSO₄ salt was dissolved in water. Temperature was maintained by hot plate attached with Magnetic stirrer and measured by thermometer. MnSO₄ was added repeatedly to the solution and stirred. The MnSO₄ solution reached saturated stage with 60 g of MnSO₄ salt added to water and the solution was stirred for two hours. The beaker contains saturated solution of MnSO₄ with PH-6 prepared at room temperature. This solution was allowed for slow evaporation at room temperature.Good quality single crystals of MnSO₄ were harvested after 23 days in different sizes, maximum up to 1.8cm x .9cm x .5cm which is shown in figure 1.a. For the growth of single crystals of L-Lysine doped manganese (II) sulphate, 1gram of L-Lysine was added to the saturated solution of $MnSO_4$ which was maintained at $50^{0}C$ to avoid decomposition. Then the solution was allowed to stir using magnetic stirrer for more than two hours. The solution was allowed to evaporate slowly at room temperature. LMnSO₄ salt was synthesized according to the reaction,

$$\begin{array}{c} MnSO_4 + HO_2CCH(NH_2)(CH_2)_4NH_2 \\ \downarrow \\ COO^-H^+ - CH - NH_2 - CH_2 - CH_2 - CH_2 - CH_2 - NH^+ - \\ Mn^{2+}SO_4^{2-} \\ + H_2SO_4 \end{array}$$

After 18 days, good quality single crystals were obtained which is named as LMnSO₄[A] in different sizes, maximum up to 1.15cm x0.3cm x0.1cm as shown in Figure 1.b. In the same way, rather than 1 gram of L-Lysine, 2 grams of L-Lysine was added to the saturated solution of MnSO₄. After 32 days the good quality crystals of LMnSO₄-[B] were grown in different sizes maximum size up to 0.7 cmx1cm x1cm.which is shown in Figure 1.c.



Figure 1.a. MnSO₄ single crystal.



Figure 1.b. MnSO₄[A] single crystal.



Figure1.c . LMnSO₄[B] single crystal.

3. CHARACTERIZATION

The grown crystals have been analyzed by different characterization techniques. The structure of grown single crystals of MnSO₄ and amino acid doped MnSO₄ was confirmed by powder crystal X-ray diffraction analysis using (SEIFERT XRD 3000P) nickel filtered CuK α radiation (36KV, 20mÅ, λ =1.5418). The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm⁻¹. The optical properties of the crystals were examined between 200 and 1100 nm using LAMBDA-35 UV-Vis spectrometer. The mechanical property of LMnSO4 crystal was studied by Vickers hardness test. The applied loads were 25, 50 and 100 grams.

3.1 Powder crystal X-ray diffraction analysis

Powdered samples of manganese (II) sulphate and L-Lysine doped manganese (II) sulphate semi organic crystals were subjected to powder X ray studies. In this, the strong observable peaks indicate the highly crystalline nature of the sample.Powder XRD reveals that intensity of the LMnSO₄[A]

and LMnSO₄[B] were found to be maximum in the direction [011]and[120] respectively . XRD patterns of the grown crystals are shown in figures 2a, 2b and 2c. The X-ray is reflected in the reflecting planes with the angle 15-70°. The powder X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameters of the grown sample. From the XRD data, it is observed that both Manganese(II)sulphate and L-Lysine doped Manganese(II)sulphate are orthorhombic. The calculated lattice parameter values of Manganese(II)sulphate and L-Lysine doped Manganese(II)sulphate are presented in table 1. The results of the present work are in good agreement with the reported values⁷. In the case of doped sample, a slight variation in the cell volume is observed. The axial angles were $\alpha = \beta = \gamma =$ 90°. This value is same for all grown crystals.



Figure 2.a. PXRD pattern of MnSO₄ single crystals.



Figure 2.b PXRD pattern of LMnSO₄[A] single crystals.



Figure 2.c. PXRD pattern of LMnSO₄[B] single crystals.

| | I | | |
|--|-------------------|------------------------|------------------------|
| compound | MnSO ₄ | LMnSO ₄ [A] | LMnSO ₄ [B] |
| a | 14.86 | 0.3754 | 0.5297 |
| b | 7.303 | 1.140 | 2.104 |
| с | 6.67 | 0.33 | 0.5169 |
| Cell volume | 723.8 | 0.1412 | 0.5761 |
| Average critical size nm | 71 | 20 | 25 |
| Average dislocation density 10 ¹⁵ | 0.1934 | 0.25 | 0.1502 |
| Average strain | 0.1878 | 0.1489 | 0.04871 |

Table 1: Lattice parameters of LMnSO₄ single crystals for various combinations

3.2 UV- Spectral Analysis

The UV - visible spectrum was recorded for the powdered sample of the crystals grown by slow evaporation . This study was carried out in the same spectral range for the grown $LMnSO_4$ crystals A and B .The recorded optical transmittance spectrum of the grown single crystals of $MnSO_4$, $LMnSO_4$ [A] and $LMnSO_4$ [B] are shown figures 3a, 3b and 3c.



Figure 3.a Optical transmittance spectrum of MnSO₄.



Figure 3.b Optical transmittance spectrum of MnSO₄ [A].



Figure 3.c Optical transmittance spectrum of LMnSO₄[B].

From above studies, the grown crystals have good optical transparency between 192 to 1100 nm. The lower cutoff value of grown crystals is above 300 nm.So the grown crystals have good optical transparency. The transmittance range of grown crystals is increasing with increase in L-Lysine percentage and the lower cut off values of grown crystals is also increasing with increase in L-Lysine percentage. So the grown crystal L-Lysine doped Manganese(II) sulphate is used for UV-applications.

3.3 FTIR analysis of grown cryatals

The FTIR spectrum was recorded for the powdered samples of the crystals grown by slow evaporation using attenuate total reflectance method in the frequency range 400-4000cm⁻¹ by a BRUKER 66 VFT-IR spectrometer. In order to make comparison,the same study was performed for $MnSO_4$ and $LMnSO_4$ crystals. The recorded FTIR spectrum for the grown crystals are shown in the figures 4.a, 4.b and 4.c. From the figures below, various absorption peaks present in the recorded FTIR spectrum for all grown crystals were assigned to their corresponding functional groups and are listed in table 2.



Figure 4.a FTIR analysis for MnSO₄ single crystals.

Table 2. FTIR spectral data of grown crystals with

standard values.

| Mode of vibrations | Standard wave Number cm ⁻¹ | MnSO ₄ | LMnSO ₄ [A] | LMnSO ₄ [B] |
|--|--|--|--|---|
| O-H stretching | 3400- 2400 | 3335 | 3399 | 3400 |
| C-H bending | 700- 610(b) | 631 | 614 | 613 |
| C-O Stretching | 1260- 1000(S) | 1101 | 1101 | 1106 |
| O-H bending | 1440- 1400 | - | 1490 | - |
| Solfonate s=O stretching | 1350- 11750 | 2180 | 2142 | 2141 |
| S-O stretching | 1000-750 | 777 | - | - |
| Metal oxides bonding | 600-500 | 464 | - | - |
| | Standard | | | |
| Mode of vibrations | wave number cm ⁻¹ | MnSO ₄ | LMnSO ₄ [A] | LMnSO ₄ [B] |
| Mode of vibrations O-H stretching | wave number cm ⁻¹ 3400- 2400 | MnSO ₄ 3335 | LMnSO ₄ [A] 3399 | 3400 |
| Mode of vibrations O-H stretching C-H bending | wave number cm ⁻¹ 3400- 2400 700- 610(b) | MnSO ₄ 3335 631 | LMnSO ₄ [A] 3399 614 | 2400 613 |
| Mode of vibrations O-H stretching C-H bending C-O Stretching | wave number cm ⁻¹ 3400- 2400 700- 610(b) 1260- 1000(S) | MnSO ₄ 33335 631 1101 | LMnSO ₄ [A] 3399 614 1101 | CMnSO ₄ [B] 3400 613 1106 |
| Mode of vibrations O-H stretching C-H bending C-O Stretching O-H bending | wave number cm ⁻¹ 3400- 2400 700- 610(b) 1260- 1000(S) 1440- 1400 | MnSO ₄ 3335 631 1101 - | LMnSO ₄ [A] 3399 614 1101 1490 | LMnSO ₄ [B] 3400 613 1106 - |
| Mode of vibrations O-H stretching C-H bending C-O Stretching O-H bending Solfonate s=O stretching | wave number cm ⁻¹ 3400- 2400 700- 610(b) 1260- 1000(S) 1440- 1400 1350- 11750 | MnSO ₄ 3335 631 1101 - 2180 | LMnSO ₄ [A] 3399 614 1101 1490 2142 | LMnSO ₄ [B] 3400 613 1106 - 2141 |
| Mode of vibrations O-H stretching C-H bending C-O Stretching Solfonate s=O stretching S-O stretching | wave number cm ⁻¹ 3400- 2400 700- 610(b) 1260- 1000(S) 1440- 1400 1350- 11750 1000-750 | MnSO ₄ 3335 631 1101 - 2180 777 | LMnSO ₄ [A] 3399 614 1101 1490 2142 - | LMnSO ₄ [B] 3400 613 1106 - 2141 - |



Figure 4.b FTIR for LMnSO₄[A].



Figure 4.c. FTIR FOR LMnSO₄ [B]

3.4 Vicker's Micro hardness study

Hardness is a measure of material's resistance to localized plastic deformation. It plays a key role in device fabrication. The mechanical property of LMnSO₄ crystal was studied by Vickers hardness test. The applied loads were 25, 50 and 100 grams. The measurement was done at different points on the crystal surface and the average value was taken as H_v for a given load.

The Vicker's micro hardness was calculated using the relation

$Hv = 1.8544 P / d^2$

Where, P - is the applied load and d- is the diagonal length of the indentation impression. The calculated Vickers hardness values for LMnSO₄ crystals as a function of load is shown in figures 5.a, 5.b & 5.c. Vickers Hardness value of LMnSO₄ crystal is grater than 1.6. It is concluded that the samples are soft materials.

VARIATIONS OF VICKER'S MICRO HARDNESS VALUES WITH APPLIED LOAD





Figure 5.a Hardness curve for MnSO₄ single crystal.







Figure 5.b Hardness curve for LMnSO₄[A] single crystal.



Figure 5.c Hardness curve for LMnSO₄[B] single crystal.



3.5 DIELECTRIC STUDY:

Optically good quality single crystals of $LMnSO_4$ were selected for dielectric measurements using LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil. Silver paint was applied on both the faces to make a capacitor with the crystal as a dielectric material. The dielectric constant is calculated using the relation

 $D = Cd / \epsilon_0 A$

Where C is the capacitance, d is the thickness, A is the area and ϵ_0 is the absolute permittivity of free space (8.854 × 10⁻¹² F/m).

The variation of dielectric constant (D)

was studied as a function of frequency for the grown crystal and is shown in Figure 6.a The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. From the figure 6.a, it is also observed that dielectric constant decreases with increase in frequency. The variation of dielectric loss with frequency is shown in Figure 6.b. The characteristics of low dielectric loss at very high frequency suggest that it possesses enhanced optical quality with lesser defects and this parameter is essential for nonlinear optical applications



Figure 6.a. Dielectric constant Vs log f.



Figure 6.b.s Dielectric loss (tan⁶) Vs log f.

4 CONCLUSIONS

The inorganic material $LMnSO_4$ was synthesized and its structure was confirmed by powder X-ray diffraction study. The size of the crystal depends on combinations of MnSO4 and L-Lysine. The [021],[011] and [120], facets are the most prominent among the other facets of the grown crystal. The determined lattice parameter values reveal that the grown crystals belong to orthorhombic system⁷. The functional groups present in the grown crystals were confirmed by FTIR spectroscopy in comparison with that of standard wavelength in the range 0f 190-1100nm.UV-vis study showed that the

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grown crystals have good optical transparency between 300-1100nm. The Vickers hardness number of the grown crystal increase with load at lower load conditions and then saturates. The calculated value of Meyer's index 'n' of the crystals is greater than 1.6 and reveals that they are soft. The dielectric measurements reveal that LMnSO₄ crystal possesses enhanced optical quality with lesser defects.

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Efficient growth techniques and properties of Benzophenone Single Crystals for NLO Applications: A Review

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Abstract: Benzophenone is one of the promising organic NLO materials for their high energy laser photonic applications and hence this review is mainly emphasized on the discussion of growth, efficiency and applications of low melting organic NLO benzophenone crystals in order to improve their structural and physical properties. To grow bulk and good quality benzophenone crystals by various techniques adopted has been discussed such as slow evaporation method, Microtube-Czochralski method, and Vertical Bridgman method. It is acknowledged that the size and the efficiency of the growing benzophenone single crystal varies with that of the techniques we are using has been discussed below. The SHG efficiency of pure benzophenone crystal also been compared with the standard KDP crystal. Also optical transparency behaviour of the benzophenone crystal has also been reviewed.

Keywords: Benzophenone, single crystals, Solution growth, Melt growth, NLO, SHG efficiency

1. INTRODUCTION

1.1 Necessity for the organic NLO

Crystals:

Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity because of the lack of extended π -electron delocalization [1] but some organic NLO crystals form a non-centrosymmetric structure which exhibit second-order nonlinear optical properties that far surpassed those of the conventional materials has now led to the synthesis and evaluation of a wide range of potentially useful solid materials which have potential applications

in signal transmission, data storage, optical switching, laser printing, displays, inflorescence, photolithography, remote sensing, chemical and biological species detection, high resolution spectroscopy, medical diagnosis and underwater monitoring & communication [2]. Thus Organic NLO materials are often superior to inorganic in terms of their response speed, optical clarity and the magnitude of their third order susceptibility and for a material to exhibit NLO activity it should be non Centro symmetric. Hence it may be useful to prepare organic crystals which have aromatic rings having high non linear optical coefficient, higher laser damage threshold, fast response, low mobility and large band gap applications [3].

1.2 Significance of the present review:

Although, organic crystals with higher nonlinear optical (NLO) efficiency have the great importance for their applications in high-energy lasers applications but it is difficult to grow the bulk crystals of pure organic materials because of their low thermal stabilities and presence of large chromophoric cations and hence the organic crystals generally grow with structural defects. To realize the full efficiency of devices based on single crystals, crystals must be free from the defects since solution growth includes lot defects also it is difficult to grow large size organic single crystals and hence by adding suitable dopants and functional groups.



Figure 1. Structure of benzophenone.

we can modify the physical properties of single crystals which tends to enhance bulk growth of organic crystals with less defects but from some literature survey tells that even by adding such dopants and functional groups may hardly control the defects in crystals and hence by adopting various growth techniques results in improvement in molecular alignment of the crystals and tend to modify the crystal quality and in its perfection. Thus in this review the mainly focused discussion is on growing large and perfect benzophenone single crystals for high-energy laser applications since it is a promising NLO material where the absorption is visible in the blue light region having a cut-off wavelength lower than 450nm [4,5,6] and it has nearly six times higher NLO efficiency than that of Potassium dihydrogen phosphate (KDP), a well-known inorganic NLO material [7,8].

Table 1. Crystal data of benzophenone.

| Empirical formula | $: C_{13}H_{10}O$ |
|-------------------|-------------------------------------|
| Formula weight | : 182.217(g·mol-1) |
| Crystal system | : orthorhombic |
| Space group | $: P2_12_12_1[9]$ |
| Boiling-point | : 305.4 °C |
| Melting-point | : 48.5 °C (α form) & 26 °C |
| | (β form) [10] |
| Density | : 1.111 at 18 °C |
| Vapour pressure | : 1.93 \times 10-3 mm Hg at 25 °C |
| Refractive index | : 1.696 at 19 °C [11] |
| Solubility | : Practically insoluble in water |
| | but soluble in organic |
| | solvents such as alcohol, |
| | ether, acetone, acetic acid, |
| | chloroform and |
| | benzene [12] |
| Flash-point | : > 110 °C |
| Stability | : Decomposes on heating to |
| | produce toxic gases; reacts |
| | with strong oxidants. |

2. GROWTH TECHNIQUES:

Since benzophenone is a promising organic NLO material due to its enormous applications [13], it is necessity to grow benzophenone with high quality and perfection crystals [14]. So from many literature surveys which had been discussed about various growth techniques such as indirect laser heated pedestal growth (ILHPG) method [15], Microtube-Czochralski (µT-CZ) method [16], seed-oriented undercooled melt growth [17], Vertical Bridgman (VB) method [18], and uniaxially solution method crystallization (USC) of Sankaranarayanan-Ramasamy [19] have been reported with the aim of growing bulk organic NLO benzophenone single crystals. Among all the above stated methods, the Microtube-Czochralski and Vertical Bridgman methods are more versatile, bulk and unidirectional crystals can be grown by optimizing the growth parameters [12].

Let we see how some of the techniques are adopted for the growth of benzophenone single crystals.

2.1 Solution Growth:

Growth of NaCl (common salt) from aqueous solutions (sea water) is considered as one of the ancient methods of solution growth in which crystals are grown by slow evaporation technique. The method of crystal growth from low temperature aqueous solution is extremely popular due to its easy way of production and technologically importance due to its cost effectiveness. It is the most widely used method for the growth of single crystals since from ancient time but the major disadvantage for growth of single crystal by low temperature solution growth may takes uncertainity period of time. It may be of weeks, months and sometimes vears. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. An external impurity, power failure or a contaminated batch of raw material can destroy months of work.

2.1.1 Slow evaporation technique:

In this solution technique by Claude et al has grown the benzophenone single crystal by taking solid flaky benzophenone salt as precursor and dissolved in ample amount of alcohol till it reaches saturation state. The solubility and supersolubility of benzophenone was observed to be 10 grams and 15 grams per 100ml of ethanol solvent. Then the supersaturated solution is kept as constant temperature solution growth process for nucleation and subsequent crystallization. As grown crystals of benzophenone were a cleaved sample of size 4.5 cm x 4.5 cm x 4 cm was the crystal of the sample crystallized using solution growth apparatus [20].

2.2 Melt Growth:

In the literature the benzophenone single crystal was first grown by the Czochralski technique [21] followed by reports of benzophenone crystals were grown from the solution method [22] and and then by Bridgmann technique [23]. There are various types of melt growth but in accordance with the literature survey only suitable method for growing benzophenone single crystal were discussed below.

2.2.1 *Microtube-Czochralski* (μ T-CZ) *growth*:

The benzophenone crystal, an organic nonlinear material was grown by Czochralski method by Bleav et al. [21] for the first time which has high imperfection with smaller dimension. Tachibana et al. [24] has grown much better than the previous benzophenone crystals by using the similar experimental setup of Bleav et al. A technical brief of the experimental setup employed in this investigation can be found elsewhere [25]. The brief description of this technique is discussed here. Highly purified benzophenone material was filled in a circular shape static glass crucible. The source material filled crucible has to be placed inside a resistive heated furnace. Commercially bought Eurotherm temperature controller with an accuracy of \pm 0.1°C should be employed to control the temperature of the furnace. Instead of seeding by pre-grown defect free seed crystal, stainless steel micro tube of micrometre size (µm) has to be used for seeding the melt. Since melt wets the inner walls of the fine capillary tube, it rose to a height, which depended by the tube radius, the surface tension of the melt, the melt density and the contact angle of the melt with micro tube. A fine column of melt raised inside the micro tube will be crystallized first due to heat dissipation through seed rod and the grown crystal inside the micro tube was acted as a seed for further growth. The growth temperature and the pulling rate of the crystal should be optimized for the growth of benzophenone single crystals. The optimizing growth parameters for the present investigation are, pulling rate: 1.0 - 1.5 mm/hr, seed rotation rate: 5-10 rpm, the cooling rate: 1°C.hr⁻¹, length of the micro tube underneath the melt surface: 1.5mm and the axial thermal gradient: 8°C/cm. Once the growth run was completed, the system temperature was reduced to room temperature (31°C) at a predefined cooling rate to avoid the thermal stress in the grown crystal.

2.2.2 Vertical Bridgman (VB) growth:

By the literature survey of (M. Arivanandhan et al.). bulk crystals of benzophenone were grown using the VB system. This VB system consists of three major parts such as transparent furnace, temperature controller and ampoule translation assembly. The transparent furnace consist a central quartz tube which is centrally placed in a glass beaker filled with two immiscible liquids. Sufficient volumes of deionized water and sunflower oil (normally used for cooking) were used for low temperature and high temperature zones respectively since the melting point of benzophenone is ~48°C. Spiral shaped tubular resistive heaters were encircled the growth tube at hot and cold zones. Commercially bought eurotherm temperature controller with an accuracy of $\pm 0.1^{\circ}$ C was employed to control the zone temperatures. Direct observation of solidliquid interface, which is more feasible in transparent furnaces than conventional furnaces, is important for the directional solidification to determine the desired interface shape by controlling the growth parameters. In the case of VB growth of organic material, due to its low thermal conductivity one has to adopt the recommended translation rate of 1-2 mm.h⁻¹ [26]. The more details of the growth processes can be found elsewhere [27].

3. RESULTS AND DISCUSSIONS:

In this section we discuss some of the literature surveys of results on the nonlinear optical properties of benzophenone single crystals which were grown by various techniques.

3.1 Optical studies:

Since for the grown benzophenone crystal to be used in optical applications should have high transmittance (%), which had been given by (A. Claude et al.) He studied the absorption spectra of benzophenone which was taken UV-VIS spectrophotometer where two prominent absorption maxima were observed at 225nm and 255nm respectively. It also has two additional maxima, one at 285nm and another at 345nm. A transmission peak at 255nm signifies a π to π^* transition and identification of the presence of the benzene rings in the radical.

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Aromatic systems, which contain p electrons, absorb strongly in the ultraviolet which fulfils the efficient properties of having high nonlinear optical coefficient, higher laser damage threshold, fast response, low mobility and large band gap and high energy laser applications [3].



Figure 2. Transmission Spectra of benzophenone (adapted from [20].)

This is evident by a previous transmission peak at 245nm and the very low transmission were observed below the cutoff wavelength and high transparency at 400-900 nm highlighted the optical property of the grown benzophenone crystal which is given below.

3.2 SHG Efficiency:

Powder SHG measurement by Kurtz method is an important and popular study to identify the conversion efficiency of grown benzophenone NLO material. The SHG efficiency of the benzophenone grown by Microtube-Czochralski (μ T-CZ) method was given by *M. Arivanandhan et al.* The measured SHG efficiency by Kurtz powder method was found to be three times higher than that of the efficiency of the standard KDP crystals [28].

4. CONCLUSION:

As to conclude this review, we have noticed that in the near future, benzophenone crystal can be grown easily, bulky with high perfection as many recent reported works attracted the researchers by some unique advantage of growing bulk and unidirectional benzophenone crystals at ambient temperature which causes minimum thermal induced grown-in defects using many experimental set-up with high conversion efficiency and high growth rate.

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Role of Polymer in Weeding and Seeding Machinery in Agriculture Rice Mechanization

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Abstract: In agricultural farm machinery, polymers are widely used for many applications. In recent years many agricultural farm implements are adopting polymer based plastic parts like seed dill ferule roller, weeding equipment, star wheel of harvester, vegetable planter hopper, zero till drill flute, animal voke, maize sheller, diary vessels etc as a step towards value engineering. By varying the synthetic blend component and its miscibility with starch, the morphology and hence the properties can be regulated easily and efficiently. Blends containing thermoplastic starch (non crystalline starch) may be blended or grafted with biodegradable polyesters, such as polycaprolactone, to increase flexibility and resistance to moisture. Blends mainly formed into films and sheets, that are used for foaming and injection molding. By mixing thermoplastic starch with cellulose derivatives, rigid and dimensionally stable injection molded articles result. Seeding and weeding in paddy is an essential component in paddy production. There are many models of seeders and single row cono weeders available in the market which are being used for mechanized seeding and weeding operation. These are basically made with Mild Steel which has certain disadvantages in terms of machinability, reproducibility, weight, life, appearance etc. An improved manually operated 8-row drum seeder (plastic moulded) for direct sowing of pre-germinated paddy for wetlands and plastic moulded cono weeder developed was evaluated for its performance in various farmers field. It was observed that the cost of production of plastic moulded eight row drum seeder and plastic moulded cones for cono weeder was almost on par to that of these equipment made with MS sheet. Field studies revealed that plastic moulded seeder and cono weeder recorded higher field capacity, seeding/ weeding index and performance index over implement made of MS, with lower working force and plant damage. The ergonomic study revealed that heart beat/min, VO₂/min, ODR score, body part discomfort score, OCR as VO₂ max, per cent of plastic moulded equipment was found better over metallic model of equipment. This clearly gave an indication that there is a scope for substitution of MS material by polymers in rice mechanization. This paper deals with production process and performances evaluation of plastic moulded cono weeder for wet land paddy production.

Key words: Rice mechanization, Polymer, cono weeder, drum seeder, molding process, Ergonomics studies.

1. INTRODUCTION:

The average productivity of rice in India, at present, is 2.2t/ha, which is far below the global average of 2.7t/ha. The productivity of rice is higher than that of Thailand and Pakistan but much

lesser than that of Japan, China, Vietnam and Indonesia (Anon., 2011). Transplanting of paddy in puddled field is generally preferred over dry sowing of seed due to severe problems of weeds. There are different types of paddy seeder are available with mild steel and aluminum material used in the part of drum which is carrying the paddy seed. The mild steel drum seeder while using day by day in wet land easily occur corrosion and reduced reliability and life of the seeder. Now a days paddy seeder are improved and modified drum with hyperboloid shaped with Medium Density Poly Urethane material used (Fig.1). Weeding is an important practice to be carried out during the initial stages of crop growth especially for controlling the weeds competing with the crop, stirring the soil for aerating the crop root zones and for burying the weeds in to the soil (Kwesi and De Datta, 1991). In India, farmers mainly follow manual hand weeding and chemical weeding. The manual weeding, which takes about 20 per cent of labour requirement in paddy cultivation is expensive and drudgeries operation (Sucheta Singh and Oliver Hensel 2012). The operation of weeding is usually performed manually with the use of bare hands/ traditional hand tools in bending position, inducing back pain. With the scarcity of labour mechanical weeding is the only solution as it is an environmentally safe alternative to herbicides for weed control. Availability of skilled labour is also scarce. To obviate this mechanical weeding is the only solution. At present there are many weeders being used in paddy. Among these, the cono weeder is the most effective and popular (Fig.2). The normal cono weeders available in the markets have the cones made of Mild Steel (MS) based on International Rice Research Institute. Philippines design. Since the cones of the cono weeders are in constant contact with the soil, the rolling resistance by the wet soil on the weeder surface creates strain on the operator while pushing this equipment. Also due to constant contact with the soil, there is a tendency to develop rust and hence hinder in the smooth operation and reduce the life of the cono weeder. Since cone is the part which comes into contact with the soil, an effort was made to use an alternative material for the cone to reduce the force required to push the weeder. Further, it was found that fabrication of cones was a tedious process and time consuming process. To make production process faster and to maintain interchangeability of parts, a production process was developed jointly by Central Institute of Agricultural Engineering, Regional Centre, in collaboration with M/s KSNM Marketing, Coimbatore, a leading manufacturer of cono

weeder (Rvindra Naik et.al., 2013 & Annamalai et.al. 2012).

2. PRINCIPLE OF CONO WEEDER:

The cono weeder is used for uprooting and burying weeds in between standing rows of rice in wetlands with the help of a set of lugs in the conical rotor/cones due to its pull and push operations. A pair of cones are placed one behind the other in an offset manner. A long handle is provided for the operation of the unit. A float is provided ahead of the pair of cones which gives buoyancy effect and prevents sinking of the unit into the wet soil during operation. During the forward movement of the operator, the weeder creates horizontal back and forth movement in the top 3 cm layer of the soil and the weeds are uprooted and buried in a single pass. It disturbs the topsoil and increases the aeration to the root zone. This helps in better root growth which in turn leads to better physiological growth, greater tillering and higher yield. A thin film of water is a prerequisite for effective operation of the cono weeder. If the soil is too dry, the cono weeder rolls over the soil surface without uprooting and burving the weeds. Cono weeder is also used to mulch the green manuring plants which are grown in the intra row spacing in paddy field. Generally, first weeding is done within 15-20 days of planting seedlings and second weeding is taken up again after 15 days. Third and fourth weeding before onset of flowering can be also taken up for the increase in yield (Ravindra Naik et.al., 2013)

3. DEVELOPMENT OF PRODUCTION PROCESS OF PLASTIC MOULDED CONO WEEDER:

To use an alternate material for the cone, polypropylene impact copolymer, manufactured by copolymerising propylene was attempted. The propylene elastomeric phase in the polypropylene impact copolymer improves the impact strength of the products, and more importantly this improved impact strength is retained even at sub-zero temperatures. The medium melt flow characteristic of copolymer grade MI1530 is especially suited for injection-moulded components in the industrial sector. The grade possesses good toughness and the articles moulded can withstand a continuous. service temperature of up to 90°C This grade meets with the requirements of Indian Standard IS: 10910 on "Specifications for Polypropylene and its copolymers for its safe use in contact with foodstuffs, pharmaceuticals and drinking water". The grade also complies with FDA regulation: CFR TITLE 21 - 177.1520, on olefin polymers. The details of production process of plastic moulded cones are given in Fig 3.

4. RESULT AND DISCUSSION

4.1 Comparison between M.S. sheet cone v/s plastic cone with M.S. sheet lugs:

From the Table 1, it is observed that the cost of pproduction of plastic moulded cones for improved cono weeder is Rs 280/cone, which is only slightly higher than m.s. sheet cones (Rs 260/cone). But there are several advantages by adopting the process for production of plastic moulded cones. It is seen that the production capacity per person per day has increased from 4 to 50 cones. Apart from this it is easy to maintain the quality of production, and the inter changeability of the component can also be achieved. The weight of the weeder has also been reduced from 7.5 to 6.1 kg (by 19 per cent). (Annamalai et.al., 2012, Ravindra Naik et. Al., 2013)

4.2. Performance evaluation of the cono weeder:

The performance evaluation of the cono weeder with plastic moulded cones (Fig. 1) in comparison with commercial model of cono weeder was taken up at lowland paddy fields in the standing crop of ADT 43 variety at Bhavanisagar, Tamil Nadu, India. During the experiment, effective field capacity, weeding index, plant damage, and performance index were determined Table. 2.

4.3. Ergonomical evaluation:

Ergonomical evaluation was carried out on selected female workers for assessing their suitability in terms of the following (Fig .4).

(*i*) Heart rate and oxygen consumption rate:

These are relevant parameters for assessing the human energy for performing various operations (Gite and Singh, 1997)

(ii) Energy cost of operation:

The energy costs of operation of the selected weeders were computed by multiplying the oxygen consumed by the subject during the trial period with the calorific value of oxygen as 20.88 kJ/l (Nag *and Dutt, 1979*)

(iii) Acceptable work load:

The acceptable workload (AWL) for Indian workers was the work consuming 35 per cent of VO_2 max (Gite and Singh, 1997 and Muthamil Selvan et.al., 2010).

(iv)Limit of continuous performance (LCP):

The extent to which a person may increase his work rate depends in part on how much he can increase his heart rate from resting level to his maximum level, because the increase in heart rate plays a major role in increasing the cardiac output from rest to maximal work (Rodahl, 1989). To have a meaningful comparison of physiological response, Δ H values (Increase over resting values) for heart rate (work pulse) was calculated (Tewari. et.al., 1991).

(v) Overall discomfort rating (ODR):

For the assessment of overall discomfort rating a 10 - point psychophysical rating scale (0 no discomfort, 10 - extreme discomfort) was used which is an adoption of Corlett and Bishop (1976) technique.

5. Conclusion:

An injection moulding process using polypropylene copolymer (PPCP) for making the cones for conoweeder has been developed. The blades are of m.s.sheet and are inserted into the

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moulded die before starting of moulding process. Field evaluation study reported that the modified cono weeder recorded better field performance, enhanced the comfort with considerable reduction in heartbeat, oxygen consumption, acceptable work load, limit of continuous performance, overall discomfort rating, body part discomfort rating. The production process had higher output per person;



Figure. 1. Eight row paddy seeder. (Ccourtesy: M/s. KSNM Marketing, Coimbatore, India)





Figure 3. Production process of plastic moulded Cono weeder (\Courtesy M/s. KSNM Marketing, *Coimbatore*, *India*)

interchangeability of parts was possible; less labour dependent and better production quality could be maintained. The study concluded that there is a tremendous scope to replace the existing m.s cones with polypropylene impact copolymer material by adopting the injection moulding production process.



Figure 2, Plastic moulded cono weeder. (Courtesy: M/s. KSNM Marketing, *Coimbatore*, *India*)



Figure. 4, Ergonomic evaluation of plastic moulded cono weeder

| Description | Commercial model | Improved model |
|-------------------------|---|---|
| | M.S Sheet cone | Plastic cone + M.S. Sheet lugs |
| Material used | m.s. sheet(1.5mm) : 1100 g | Polypropylene : 750g m.s. sheet (2mm): 750g |
| M.S Welding cost | Rs 120 (4 cones/ day/welder) | NIL |
| Injection moulding cost | NIL | Rs 60/ cone |
| Material cost | Rs 140/ rotor | Polypropylene : Rs 120 M.S. Sheet (2mm): Rs 100 Total : Rs 220 |
| Total cost | Rs 260/cone | Rs 280/cone |
| Output/day/ worker | Four cones | Fifty cones |
| Major Differences | Production rate is less No consistency in quality More labour dependent | More pieces can be manufactured per unit time Quality can be maintained Life of cones is expected to increase Less labour dependent Interchangeability of the component |

 Table 1. Comparison between m.s. sheet cone v/s Plastic cone with m.s sheet lugs (Annamalai, et.al 2012)

| Table 2. | Field performance | of cono weeders | under investiga | ation.(Ravindra | a Naik et.al., 2013) |
|----------|-------------------|-----------------|-----------------|-----------------|----------------------|
|----------|-------------------|-----------------|-----------------|-----------------|----------------------|

| | Difference over | | |
|------------------------------------|-------------------|--|--------------------------------|
| | Commercial weeder | Cono weeder with plastic moulded cones | commercial weeder, per cent |
| Effective Field capacity , m^2/h | 190.0 | 265.00 | 28.30 |
| Weeding index, per cent | 75.2 | 81.1 | 7.04 |
| Pushing Force, N | 43.3 | 37.50 | - (13.39) |
| Plant damage, per cent | 6.1 | 5.90 | - (3.27) |
| Performance Index | 1358.1 | 2031.90 | 49.61 |
| Weight, kg | 7.5 | 6.1 | - (18.6) |

| | Type of weeder | | | | |
|-----------------------------|---------------------------|---------------------------------------|--------------------------------|--|--|
| | Commercial cono weeder | Cono weeder with plastic mouded cones | commercial weeder, per cent | | |
| Heart beat/min | 162 | 128.80 | - (20.43) | | |
| VO ₂ /min | 1.45 | 1.27 | - (12.41) | | |
| ODR Score | 6.2 | 5.50 | - (11.29) | | |
| Body part discomfort score | 39.4 | 26.34 | - (33.14) | | |
| OCR as VO_2 max, per cent | 83.4 | 76.2 | - (8.63) | | |
| Energy grade | Heavy | Heavy | | | |
| Rest pause, min | 12.9 | 10.5 | - (18.60) | | |

Table3. Ergonomic evaluation of operator using two models of cono weeders (Ravindra Naik et.al., 2013)

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Development of Electromagnetic Shielding Wearable Electronic Textiles using Core Conductive Fabrics

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Abstract: Today wearable electronics are playing a vital role in many applications such as Military, Medical application, telecommunications and health care garments. Conductive textiles also provide wide range of applications in areas of civilian and military purposes. In this research work an attempt has been made to design and develop core-sheath conductive varns with copper filament and optical fibre as core and cotton as sheath using Dref-3 Friction spinning system. The special guide mechanism has been designed and used to produce uniform structure of core-sheath conductive yarns. Three different core-sheath ratios such as 67/33, 80/20 and 90/10 respectively, were produced by varying the draft in the second drafting unit which fed the cotton carded slivers to cover the core component. Copper filament of 38 SWG British Standard Gauge has been used as core component. The nominal count of core-sheath conductive yarn produced in this research was 328 tex and core component kept as constant 261 tex for all the yarn samples. Optical core conductive yarns are produced by using CK-20 type optical fibres. The process parameters such as perforated drum speed and yarn delivery speed are 4000 revolution per minute and 70 metres per minute respectively, kept as constant for all the samples. The copper core conductive yarns were used to develop the conductive fabrics. These fabrics have very good scope for many applications for development of electromagnetic shielding wearable textiles, mobile phone charging and body temperature sensing garments. It also has the optical fibre core conductive yarns which were used for the development of signal transferring garment for telecommunication and data transferring purpose. In this work two sensors have been integrated in sensorized garments for monitoring the body temperature. Moreover, it has been pointed out the use of these sensorized garments as a valid alternative to existing instrumentations which are in several health care areas. The results on the copper core conductive yarns and Optical core conductive yarns have studied. The characteristics of core conductive fabrics such as air permeability, tensile strength, electromagnetic shielding effect, aerial density, and fabric cover factor have been analysed. The performance of the conductive fabric garment has been briefly reported. The copper core conductive yarn, Optical core conductive yarn, copper conductive fabric and conductive fabric garment have the very high potential which is to be commercialized.

Keywords: shielding fabric; core conductive fabric Electronic textiles; copper conductive; Electromagnetic shield

1. INTRODUCTION

Outline of friction spinning system, the fibres from the sliver after pre-opening and individualization are deposited in a suitable form by an air current into the gap between two cylindrical drums rotating in the same direction [1]. Either one or both the drums are perforated and have a suction arrangement inside them to restrain the fibres while they are rolled and twisted. The yarn is formed by the frictional forces between the fibres and the rotating cylindrical surfaces and is withdrawn at right angle to the direction of moving surface. Since the drum diameter is many times higher than the yarn diameter, each revolution of drum imparts a large number of turns to the yarn [2]. Dref-3 is a development over Dref-2 for improving the quality of yarn, productivity and core-sheath yarn production. Core-sheath yarn is made to improve the quality of yarn by laying part of the fibres in an aligned fashion along the direction of yarn axis in core. The remaining fibres are wrapped round the core fibres. The sheath fibres are attached to the core fibres by the false twist generated by the rotating action of the drums [3]. Two drafting units are, therefore, used in the system, one for the core fibres and other for the sheath material. After drafting in the first unit, the core filament copper fed to nip between the spinning drums in a direction parallel to the axis of the drums. The sheath fibres after passage through the second drafting unit and are deposited over core filaments by the air stream and wrapped over the core by the rotating action of the drums [4,5]. The

properties of friction -spun yarns, ring-spun yarns and other yarns spun on modern spinning systems have been compared by several authors [7-12] and the findings have been at times divergent because of the differences in raw material and processing conditions. Padmanabhan and Ramakrishnan [8] found that the filament core Dref-3 spun yarn is stronger than 100% cotton varn and cotton core yarn by about 13% and 20% respectively. Perumalraj et al [14] also reported the production of core-sheath Dref-3 friction spun yarn made out of cotton and polyester sheath and 820 denier copper filaments as core for development of electromagnetic shielding. Many applications in e-textiles have been pointed out by many researchers [15-19] for development of sensor wears, electromagnetic shielding and tele communication using conductive yarns. Ching-wen Lou [24] et al developed a complex core spun yarn using stainless steel as core in the ring spinning system. Also he point out the yarn structure made out of this system not uniform to get perfect core-sheath yarn structure. Wireless communications are impacting all areas of the military, from logistics and training to collaboration and medical support. In military offices, wireless communications keep people mobile, with continual access to information anywhere, any time. Laptop computer users attending meetings and conferences now maintain instant access to data files and internet searching so they can obtain immediate answers to questions raised. Outside the office, mobility increases productivity by allowing users to work in previously unproductive situations, such as while

traveling or wailing for appointments [20]. An attempt has been taken for development of core-sheath conductive yarn using Dref-3 spinning system, using copper filament (328 tex) as core and MCU cotton fibres (32 mm staple length) as sheath to produce three different blend ratios of 33/67, 20/80 and 10/90. Further Electro-Mechanical properties of these core-sheath Dref-3 conductive yarns are examined and reported. The Optical core conductive yarns also been produced in the Dref-3 friction spinning system and the garment has been made for signal transferring and telecommunication.

2. MATERIALS AND METHODOLOGY

In this chapter, the various materials used for this research work to produce Copper core conductive yarns, Optical core conductive yarns, Copper conductive fabrics and Optical conductive fabrics have been reported. It also dealt with the methodology adopted to produce the products and testing the same.

2.1 Materials

The core and sheath components used for manufacturing of conductive yarns are given below:

I. Copper core conductive yarns: In this research work, 38 SWG (British standard wire gauge) copper filament and MCU-5 cotton fibres were used as core material and sheath material respectively.

II. POF core conductive yarns: In this research work, two types of Plastic Optical Fibres (POF) were used as core materials namely ESKA and CK-20 which has diameter of 500 μ m and 1000 μ m respectively and MCU-5 cotton fibres as sheath material.

2.2 Methods

The Fehrer AG type DREF-3 friction spinning machine was used to produce three different core-sheath ratios of conductive yarns. Four cotton carded slivers were fed in the first drafting unit and each sliver has 4.22 grams per metre and silver irregularity value U% - 3.8, respectively. The core material (Copper filament- 261 tex) was fed in the first drafting unit with special guides. The guide device was designed and installed on the first drafting unit to increase the stability of spinning of the metal yarn. The process parameters of Dref-3 spinning machine such as perforated drum speed and varn delivery rate were set at 4000 revolutions per min and 70 m/min respectively, to produce uniform yarn structure and which has the nominal yarn count of 328 tex. By varying the draft in the second drafting system, three different coresheath ratios such as 67/33, 80/20 and 90/10 were produced. The yarn formation in the DREF-3 friction core spun yarn are carried out and for this research work, conductive yarns were produced which has three different core-sheath ratios. During the spinning process, the copper filament was fed from the first drafting unit with special guides. The guide device was designed and installed on the first drafting unit to increase the stability of spinning of the conductive yarn. The special care was taken while wrapping copper filament by adjusting the perforated drum speed, yarn delivery rate and draft in second drafting unit to produce uniform yarn structure.

2.3 Design and Development of Copper Core Conductive Fabrics

The copper core conductive fabrics are produced using power loom with copper core conductive yarns as warp and weft threads. The physical characteristics of these core conductive fabrics will be discussed in this paper.

2.4 Design and Development of Optical Core Conductive Fabrics

The optical core conductive fabrics are produced using power loom with optical core conductive yarns as weft threads and 2/60s Ne cotton threads as warp threads. The optical core conductive fabrics of ESKA & CK-20 type optical fibres respectively. The physical characteristics of these fabrics will be discussed.

2.5 Material Testing

The physical characteristics of conductive yarns and fabrics are tested as per standard testing procedures. The testing methodology & procedures are given below.

2.5.1 Yarn Testing

The yarn count, tenacity & breaking elongation and electrical properties were tested for copper core conductive yarns. The testing procedures of above tests will be discussed in this paper.

2.5.2 Fabric Testing

The fabric thickness, aerial density, cover factor, tensile strength, air resistance and electromagnetic shielding effectives were tested for copper core conductive yarns. The testing procedures of above tests will be discussed.

3. APPLICATIONS OF CONDUCTIVE FABRICS

In this chapter the various applications of conductive fabrics made out of copper core conductive yarns and optical core conductive yarns have been reported.

3.1 Copper Core Conductive Fabrics

The applications of copper core conductive fabrics made out of copper core conductive yarns as warp and weft threads are given below:

- Electromagnetic shielding garment for defence personnel
- Mobile phone charging wearable electronics development.
- Body temperature sensing garment
- The copper core conductive yarns are used for development of conductive fabrics. In this project two different woven fabric constructions were made to analyze the electromagnetic shielding effectiveness.
- Today smart garments are playing vital role and popular in the e-textiles. These garments are developed with integrated circuits and operating at very low voltages. Many researchers are developing the smart garments with thin film technology and solar power circuits.
- The another application of these conductive fabrics are usable for sensing the body temperature and it can be applicable for medical scanning purpose and heath care areas.

3.2 Optical Fibre Core Conductive Fabrics

The applications of optical core conductive fabrics made out of plastic optical fibres (POF) optical core conductive yarns as weft threads are given below:

- ✤ Tele-garment for signal transferring
- Protective garment for defence
- Garment made for body temperature sensing and mobile phone charging (dual purpose) for defence personnel



In this research work, Garment was designed shown in plate 1 with integrated circuit and sensors for body temperature sensing and mobile phone charging (dual purpose) for defence personnel. The garment has designed and embedded with two internal temperature sensors with I/C.

4. RESULTS AND DISCUSSION

In this chapter the various test results obtained by copper core conductive and optical core conductive yarns have been reported such as Contribution ratio of core-sheath components, Tenacity and breaking elongation and electrical properties. Also the electro-mechanical characteristics of conductive fabrics made out of copper core yarn and optical core yarns have been reported

4.1 Contribution Ratio of Core-Sheath Components

The core and sheath contribution and core-sheath interaction factors to tenacity are derived from the following equations [13]:

Core contribution factor (CC_T), $\% = (X/Z) \times 100$ Sheath Contribution factor (SC_T), $\% = (Y/Z) \times 100$ Core-sheath interaction factor (CSI_T), $\% = [(Z-X-Y)/Z] \times 100$

Where X, Y and Z represent the tenacity of the individual core component and parent Dref-3 yarn, respectively. The fibre strength exploitation is represented as the ratio of tenacity of yarn, core, or sheath component to fibre tenacity, expressed as a percentage.

| Sample | Core | Sheath | Parent | contr | ibution |
|----------|--------|--------|--------|-------|---------|
| code | | | yarn | | % |
| | Copper | Cotton | | | |
| | (gpm) | (gpm) | (gpm) | Core | Sheath |
| Sample A | 0.261 | 0.13 | 0.391 | 66.75 | 33.25 |
| Sample B | 0.261 | 0.058 | 0.319 | 81.82 | 18.18 |
| Sample C | 0.261 | 0.026 | 0.287 | 90.94 | 9.06 |

 Table 1. Structural parameters of parent dref-3 friction spun yarn and core-sheath components.

Note: gpm- grams per metre

Table 2. Parent dref-3 linear density and diameter of coresheath components.

| | sneuth | compone | nus. | | |
|----------------|--------------------|----------------|---------------------|--------------------|--|
| Sample code | Diamete | er, mm | linear density, tex | | |
| | Copper filament | Parent yarn | Parent yarn | Copper filament | |
| Sample A | 0.1524 | 0.738 | 391.05 | 261 | |
| Sample B | 0.1524 | 0.667 | 319.36 | 261 | |
| Sample C | 0.1524 | 0.632 | 286.65 | 261 | |

4.2 Tenacity and Breaking Elongation

The tensile properties of the parent conductive Dref-3 yarn and their core and sheath components are determined using USTER TENSORAPID Model 3 v7.0. The yarn gauge length and traverse speed of the instruments was set at 500mm and 5000 mm per min respectively. The breaking tenacity and elongation % of conductive yarns are tested. It is clear that the major strength of yarn is being shared by core portion and sheath portion, due to their different structural parameters of the sheath component. It is also evident from Table 2 that with increased blend ratio of sheath component, contribution of the core component in tenacity values shows increasing trend.

Table 2. shows that the breaking elongation of the individual sheath component for all the samples are almost of a magnitude similar to that of the parent Dref-3 yarn, whereas in the case of the core component it breaks immediately. It is also observed that the sample A (67/33 core-sheath ratio) shown improved elongation to break when compare to other core-sheath yarns due to improvement in core-sheath interaction (CSI_T-21.22%).

4.3 Electrical Properties

Electrical properties of core-sheath conductive Dref-3 spun yarns such as electrical resistance and current in amps are measured at different applied voltage of 6v, 12v and 24v. The values are given in Table 3. It shows that the electrical resistance of conductive yarns is varying according to the length of the yarn and current in amps also directly proportional to the applied voltage. The current values of conductive yarns are decreasing in trend as the yarn length increases; it is due to increasing electrical resistance of the conductive yarns.

| Conductive Yarn | Electrical Resistance, | Applied voltage 6V | Applied voltage 12V | Applied voltage 24V |
|--------------------|---------------------------|--------------------------|---------------------------|---------------------------|
| length, m | MΩ | Current (µA) | Current (µA) | Current (µA) |
| 0.5 | 0.06 | 100 | 200 | 400 |
| 1 | 0.1 | 60 | 120 | 240 |
| 2 | 3 | 2 | 4 | 8 |
| 5 | 20 | 0.3 | 0.6 | 1.2 |
| 10 | 28 | 0.21 | 0.42 | 0.84 |

Table 3. Electrical properties of core-sheath conductive dref-3 spun yarn

4.4 Physical Characteristics of Conductive Fabrics Made Out Of Copper Core Yarn and Optical Core Yarns

The Physical characteristics of conductive fabrics such as aerial density, fabric cover factor, ends per inch, picks per inch, fabric strength, fabric thickness and air resistance values are made as per standard test procedures. The two different structures of copper and optical core conductive fabrics are produced and the particulars of fabric thickness and air permeability have also reported.

4.5 Electromagnetic Shielding Tests:

Electromagnetic shielding is the process of limiting the coupling of an electromagnetic field between two locations. The shielding can be achieved using a material acting as a barrier. The EMSE of the conductive fabric was measured as per ASTM D4935-99 Test method for measuring the electromagnetic shielding effectiveness of planar materials with the given set up.



Figure 1. EMSE vs frequency of conductive fabrics.

The electromagnetic shielding effectiveness of the copper conductive fabrics are made and the effectiveness was

measured between the ranges of 560 MHz and 9.22 GHz. The figure 1 shows an attenuation of about 32dB on an average for all frequencies from 760- 860 MHz for both sample A (CCY-warp and weft) and sample B (CCY-weft only). It can also be inferred from the graph that the sample A with core-sheath ratio of 67/33 exhibits a highest shielding effect in the range 760-860 MHz. It is suggested that the sample A and B can be used to shield television, computers and similar equipments and also shielding effectiveness of the fabrics can be contributed to the fact that the electrical property of the material varies depending upon the frequency. So it is suggested to use the fabric at frequencies where higher attenuation is obtained. The shielding effectiveness can be increased further by increasing the cover factor of the fabric.

5. CONCLUSION

Through this research work the following conclusions have been made:

- The copper core conductive yarns were produced using Dref-3 friction Spinning System with Copper filament of 261 tex as core and MCU-5 cotton fibres as sheath. For the above core-sheath yarn manufacturing, a special guide mechanism has been developed to maintain the copper filament tension and to produce uniform yarn structure.
- Three different core-sheath ratios of 67/33, 80/20 and 90/10 were used to produce copper core conductive yarns by varying the draft in the second drafting unit. Among the three core-sheath ratios, the 67/33 core-sheath conductive yarn has the highest tenacity of 3.27 cN/tex and elongation to break 5.27% when compare to other core-sheath ratios. The technical reason for the same is because of its better core-sheath interaction factor CSI_T 21.22%. It is also observed that the core-sheath interaction factor CSI_T 21.22%. It is also observed that the core-sheath component was found low core-sheath interaction factor CSI_T 9.21% which causes the lower breaking tenacity and elongation percent.
- The optical core conductive yarns were produced using Dref-3 Spinning System with ESKA & CK-20 type plastic optical fibres (POF) as core and MCU-5 cotton fibres as sheath.
- The interaction of core-sheath behavior and mechanical properties of the Dref-3 conductive yarn are mainly depends upon the frictional characteristics and the percentage of core-sheath components. The electrical properties of these conductive core yarns have been studied at three differed applied voltages of 6v, 12v and 24v. It is found that the core-sheath yarns have very low resistance ranges $3-28 \text{ M}\Omega$.
- The copper core conductive fabrics and optical core conductive fabrics were produced using the copper core conductive yarns and optical core conductive yarns.
- The electro-mechanical characteristics of these conductive fabrics are studied.
- A sensorized and signal transferring garment has been designed and developed using the copper and optical core conductive fabrics for monitoring the body temperature, mobile phone charging and signals transferring. The performances of sensorized and signal transferring garment have also studied.

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Analysis of Slotted Counter Sunk (35NCD16 Steel) Aerospace Fasteners

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Abstract: Fasteners form the integrating elements of any aerospace hardware and provide the required mechanical integrity. Various types of fasteners including screws, rivets, bolts, pins, blind rivets, blind bolts, anchor nuts, solid inserts, collars etc. are used in aerospace application. Aerospace fasteners needs to be more durable, lighter and shall withstand high loads, vibrations and hostile environments such as deep space etc. In order to achieve this, aerospace fasteners are processed through specialized forging, heat treatment and thread rolling. Finite element analysis is done simulating the tensile testing of slotted counter sunk head screws and experiments are also conducted to verify the analysis results. A comparison is made on the stress distribution contours of slotted 120 degree countersunk head screw and slotted 90 degree countersunk head screw.

Keywords: fasteners; aerospace; countersunk; screws; stress distribution; finite element analysis;

1. INTRODUCTION

Joining by mechanical fasteners is common in assembly of structural components. The most important elements in structures (especially aerospace structures) are bolted joints, which are used in very large numbers on modern aircraft nowadays.

The 35NCD16 (3.5Ni–1.5Cr–0.5Mo) steel in hardened and tempered condition is widely used as fasteners in aerospace structures. The 35NCD16 steel is used for making fasteners meeting the specified axial tensile stress rating of 1250 MPa.

Slotted 120 degree CSK and slotted 90 degree CSK fasteners are tensile tested for evaluating the UTL. Analysis is carried out using a finite element analysis software Abaqus by importing a solid model of the specimen created in CATIA. A comparison is made on stress distribution and breaking loads of slotted countersunk fasteners by FE analysis.

2. MATERIAL

The 35NCD16 is a high strength, low alloy vacuum arc remelted steel that takes its name from French industry designation. The combination of high strength, toughness and superior cleanliness available with 35NCD16 VAR steel readily identify it as a candidate for aerospace structural applications. The chemical composition of 35NCD16 is given in Table 1.

| | С | Mn | Si | Ni | Cr | Mo |
|------|-------|-------|-------|-------|-------|--------|
| Spec | 0.30- | 0.30- | 0.15- | 3.50- | 1.60- | 0.35 - |
| _ | 0.40 | 0.60 | 0.40 | 4.20 | 2.00 | 0.60 |

3. SOLID MODELING

Modelling was done using CATIA V5.0. Slotted CSK head screws of dimensions M3, M4, M5 and M6 were modelled for both 120 degree and 90 degree types.

A typical solid model of a slotted 120 degree CSK screw is shown in figure 1.



Figure 1. Screw modeled using CATIA V5.0

4. FINITE ELEMENT ANALYSIS

Finite element method (FEM), one of the most accurate numerical solution methods, has been increasingly used for modelling operations. It gives accurate results and therefore, it is now a well-accepted numerical method.

Slotted CSK screws modelled and saved as STEP format using CATIA V5.0 were imported to ABAQUS/CAE 6.10 for finite element program and divided into finite elements.

The screws were regarded as having linear elastic isotropic properties and its values were entered through material properties icon. The stress strain data are entered as true stress and true plastic strain. The true stress and true plastic strain were calculated as shown below.

To convert the nominal stress to true stress, use the following equation

$$\sigma_{\text{true}} = \sigma_{\text{nom}}(1 + \epsilon_{\text{nom}})$$

To convert the nominal strain to true strain, use the following equation

 $\epsilon_{\text{true}} = ln(1 + \epsilon_{\text{nom}})$

To calculate the modulus of elasticity, divide the first nonzero true stress by the first nonzero true strain.

Young's Modulus, $E = 196589 \text{ N/mm}^2$

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To convert the true strain to true plastic strain, use the following equation

$$\epsilon_{\text{plastic}} = \epsilon_{\text{true}} - \frac{\sigma_{\text{true}}}{E}$$

The tabulated results are as follows.

Table 2. True stress and Plastic strain tabulation.

| $\sigma_{\rm nom}$ | € _{nom} | 1+ | σ_{true} | €true | σ_{true} | € _{plastic} |
|--------------------|------------------|------------------|-----------------|--------|-----------------|----------------------|
| | | € _{nom} | | | E | |
| 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 1169 | 0.006 | 1.006 | 1176 | 0.0059 | 0.0059 | 0 |
| 1200 | 0.008 | 1.008 | 1209 | 0.0079 | 0.0061 | 0.0018 |
| 1225 | 0.010 | 1.010 | 1237 | 0.0099 | 0.0062 | 0.0036 |
| 1250 | 0.017 | 1.017 | 1271 | 0.0168 | 0.0064 | 0.0103 |
| 1275 | 0.029 | 1.029 | 1311 | 0.0285 | 0.0066 | 0.0219 |
| 1300 | 0.046 | 1.046 | 1359 | 0.0449 | 0.0069 | 0.0380 |
| 1325 | 0.089 | 1.089 | 1442 | 0.0852 | 0.0073 | 0.0779 |
| 1329 | 0.121 | 1.121 | 1489 | 0.1142 | 0.0075 | 0.1066 |

Boundary conditions were applied by fixing head portion of the screw and tensile load was applied on the base of the screw as uniformly distributed load along the fastener axis as shown in fig. 2.



Figure 2. Modeled screw subjected to UDL along the axis.

Specified Ultimate tensile load = UTS x Tension Cross-section Area

| Thread diameter (mm) | Pitch | Minimum Tensile load at CSK head (KN) |
|----------------------------|-------|---|
| 3 | 0.5 | 5.0 |
| 4 | 0.7 | 8.8 |
| 5 | 0.8 | 14.2 |
| 6 | 1.0 | 20.1 |

| Toble 2 Minimum | Toncilo | Loodo | + CCV | hood | 11 |
|--------------------|---------|--------|-------|------|----|
| Table 5. Millinnum | rensne | Luau a | n con | neau | 1. |

3 dimensional 4 node tetrahedron structural solid element (C3D4) with linear displacement behaviour was used as the element type. A mesh sensitivity study was conducted before selecting the final mesh and element size. A uniform finer mesh was used throughout the length of slotted CSK screw. A typical screw model after meshing is shown in Fig. 3.



Figure 3. Meshed Model.

5. MATERIAL TESTING

Samples of fasteners were tension tested in Universal Testing Machine and the breaking load was noted. The fracture of fasteners during tensile test for all 120 deg CSK head occurred only in the head and for all 90 deg CSK head occurred in the thread. Loading is done parallel to fastener axis.

The breaking loads were tabulated from the tension tests for Slotted 120 degree CSK and Slotted 90 degree CSK for different sizes. Five samples of Slotted 120 degree and 90 degree CSK screws were tension tested. Average values of breaking loads obtained are shown in Table 6.



Figure 4. Tension testing of fasteners using Universal Testing Machine.



Figure 5. Slotted CSK screws after failure. 6. RESULTS AND DISCUSSIONS

The fracture of fasteners during tensile test occurred in the head-shank portion for 120 deg CSK fasteners while 90 deg CSK fasteners failed along the thread. The finite element analysis using Abaqus also shows presence of maximum value of stress in the shank or thread portion. Maximum stress as expected develops along the least area. In figure, red portion shows the maximum principal stress developed. For same load and same dimension of Slotted screws, 120 degrees and 90 degrees shows variations in stress distribution. The maximum principal stress developed in 120 degree CSK screws are much higher compared to 90 degree CSK screws. Pressure load corresponding to slotted 90 degree CSK screws applied in tension testing was given in FE analysis.



Figure 6. Slotted 90 degree CSK Head Screws at breaking load (Dimension: M3, Applied Load = 1109 N/mm²)



Figure 7. Slotted 120 degree CSK Head Screws at breaking load (Dimension: M6, Applied Load = 1109 N/mm²)

Table 4. M3 Slotted CSK Head screw.

7. LOAD-DISPLACEMENT RESULTS

| Load (KN) | Displacement (mm) | | |
|-----------|-------------------|----------------|--|
| | 90 degree CSK | 120 degree CSK | |
| 0.00 | 0.0000 | 0.0000 | |
| 0.12 | 0.0004 | 0.0005 | |
| 0.48 | 0.0020 | 0.0023 | |
| 1.30 | 0.0053 | 0.0063 | |
| 2.13 | 0.0088 | 0.0104 | |
| 2.96 | 0.0124 | 0.0148 | |
| 3.79 | 0.0162 | 0.0198 | |
| 4.61 | 0.0204 | 0.0258 | |
| 5.44 | 0.0249 | 0.0335 | |
| 6.27 | 0.0424 | 0.0603 | |
| 6.90 | 0.1413 | 0.1882 | |



Figure 8. Load-displacement plot for M3 Slotted CSK screw.

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| Table 5. N | M4 Slotted | CSK Head | l screw. |
|------------|------------|----------|----------|
|------------|------------|----------|----------|

| Load (KN) | Displacement (mm) | | |
|-----------|-------------------|-------------|--|
| | Slotted 90 | Slotted 120 | |
| 0.00 | 0.0000 | 0.0000 | |
| 0.48 | 0.0013 | 0.0015 | |
| 1.15 | 0.0031 | 0.0036 | |
| 2.22 | 0.0060 | 0.0070 | |
| 3.28 | 0.0089 | 0.0104 | |
| 4.34 | 0.0120 | 0.0140 | |
| 5.41 | 0.0151 | 0.0177 | |
| 7.53 | 0.0217 | 0.0268 | |
| 8.60 | 0.0255 | 0.0324 | |
| 9.66 | 0.0295 | 0.0394 | |
| 10.63 | 0.0374 | 0.0524 | |



Figure 9. Load-displacement plot for M4 Slotted CSK screw

| Table 6. M5 | Slotted CSK | Head screw. |
|-------------|-------------|-------------|
|-------------|-------------|-------------|

| Load (KN) | Displacement (mm) | | |
|-----------|-------------------|----------------|--|
| | 90 degree CSK | 120 degree CSK | |
| 0.00 | 0.0000 | 0.0000 | |
| 0.48 | 0.0011 | 0.0013 | |
| 1.19 | 0.00273 | 0.0033 | |
| 2.78 | 0.0063 | 0.0077 | |
| 4.80 | 0.0110 | 0.0133 | |
| 6.82 | 0.0156 | 0.0192 | |
| 8.84 | 0.0205 | 0.0253 | |
| 10.85 | 0.0256 | 0.0322 | |
| 12.87 | 0.0311 | 0.0401 | |
| 14.89 | 0.0370 | 0.0497 | |
| 16.81 | 0.0444 | 0.0634 | |


Figure 9. Load-displacement plot for M5 Slotted CSK screw.

| Table 7. Mo | Slotted | CSK | Head | screw. |
|-------------|---------|-----|------|--------|
|-------------|---------|-----|------|--------|

| Load (KN) | Displacement (mm) | | |
|-----------|-------------------|----------------|--|
| | 90 degree CSK | 120 degree CSK | |
| 0.00 | 0.0000 | 0.0000 | |
| 0.22 | 0.0004 | 0.0005 | |
| 0.64 | 0.0013 | 0.0016 | |
| 1.58 | 0.0032 | 0.0039 | |
| 3.69 | 0.0076 | 0.0093 | |
| 6.81 | 0.0140 | 0.0171 | |
| 9.93 | 0.0207 | 0.0254 | |
| 13.05 | 0.0275 | 0.0347 | |
| 16.17 | 0.0349 | 0.0455 | |
| 19.30 | 0.0429 | 0.0587 | |
| 22.29 | 0.0513 | 0.0765 | |



Figure 10. Load-displacement plot for M6 slotted CSK screw.

Slotted 120 degree screws showed higher displacements compared to Slotted 90 degree CSK screws and there was a

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steady increase in displacement values as for higher dimensions. Fig. 7 shows that for M3 displacement values for 120 degree and 90 degree CSK are closer while in fig.10, a higher gap can be noticed between the two.

8. COMPARISON OF FEA RESULTS WITH MECHANICAL TESTING

| Table 8. | Calculation | of breaking | load | from | FEA |
|----------|-------------|-------------|------|------|-----|
|----------|-------------|-------------|------|------|-----|

| | M3 | M4 | M5 | M6 |
|---|------|-------|-------|-------|
| Breaking load for 90 degree (tension test) (KN) | 6.91 | 10.64 | 16.82 | 22.30 |
| Tensile pressure load for 90 degree screws (N/mm ²) | 1373 | 1211 | 1189 | 1109 |
| Breaking load for 120 degree (tension test) (KN) | 3.38 | 8.04 | 11.99 | 14.85 |
| Tensile pressure load for 120 degree screws N/mm ² | 671 | 915 | 844 | 738 |
| Tensile pressure load values for 120 degree screws from FEA(N/mm ²) | 744 | 927 | 895 | 796 |
| Breaking Load for 120 degree from FEA (KN) | 3.74 | 8.13 | 12.70 | 15.99 |

Table 8. showed that both the breaking loads obtained by mechanical testing and finite element analysis were close even though the values obtained by FEA were slightly higher.



Figure 11. Tension test and FEA comparison.

Fig. 11 confirmed that the finite element analysis and mechanical testing done have a good correlation.

9. CONCLUSIONS

Even though a lot of researches regarding the material used (35NCD16 steel) for fasteners have been done, only few studies were reported on CSK screws. This paper attempts a detailed study on the finite element analysis of Slotted Counter Sunk Head Screws.

- Analysis of Slotted Counter Sunk Head Screws revealed deformation across the cross section on applying uniaxial tensile load.
- (2) An increase in Displacement values for Slotted 120 degree CSK head screws have been found compared to Slotted 90 degree CSK head screws for same dimensions and same load.
- (3) Failure occurs at head to shank portion by uniaxial tensile test which is supported by the analysis where maximum stress is shown to be developed at same region.
- (4) The uniaxial tension test results confirm breaking load needed for Slotted 90 degree CSK head screws are higher than Slotted 120 degree CSK head screws.

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Growth and Characterisation of a New Semi–Organic Nonlinear Optical TTMZS Single Crystal

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Abstract: A new semi-organic nonlinear optical crystal called Tris Thiourea Magnesium Zinc sulphate (TTMZS) was synthesized. TTMZS single crystals were grown from an aqueous solution using the Slow Evaporation method. The solubility of TTMZS was determined for various temperatures. Single Crystal X-ray Diffraction (XRD) study was carried-out to identify the lattice parameters. Various diffracting planes of the grown crystal were identified from the powder XRD study. Fourier Transform Infrared (FT-IR) studies confirm the various functional groups present in the grown crystal. The transmission spectrum of this crystal shows that the lower cut off wavelength lies at 280 nm. The thermal analysis confirmed that the crystal is stable up to 248.46°C. The Nonlinear Optical (NLO) property of the grown crystal has been confirmed by Kurtz powder Second Harmonic Generation (SHG) test.

Keywords: Crystal growth; Crystal Structure; X-ray Diffraction; Semi-Organic Material; Nonlinear Material

1. INTRODUCTION

Nonlinear Optical (NLO) crystals have great technological significance in the fields of Opto Electronics, Digital Signal Processing, Instrumentation and Optical Communication [1, 2]. In the recent years semi-organic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, low damage threshold and high mechanical strength as compared to their organic NLO counterparts. In semi-organic materials the organic ligand is attached to the inorganic host by an ionic bond. Therefore semi-organic crystals have higher chemical stability and mechanical strength compared to their inorganic counterparts [3]. Among semi-organic NLO materials, the metal complexes of thiourea have a low UV cut-off wavelength. This feature of Thiourea finds significant application in the fields of High Frequency Conversion and Second Harmonic Generation [4-8]. Thiourea being a naturally centro-symmetric molecule doesn't exhibit NLO properties; however when it forms complexes with metal ions, it NLO characteristics. Zinc Thiourea Sulphate (ZTS) is an already-reported NLO material for type II Second Harmonic Generation. It is nearly 1.2 times more nonlinear than KDP [9]. Some of the efficient NLO crystals of metal organic complexes of thiourea such as Zinc Thiourea Chloride (ZTC) [10], Bis Thiourea Cadmium Chloride (BTCC) [11] and Tris Thiourea Magnesium Sulphate (MTS) [12] have already been reported. In this communication, a new metalorganic NLO crystal of Tris Thiourea Magnesium Zinc Sulphate TTMZS is reported for the first time and the grown crystals have been characterized by various techniques.

2. EXPERIMENTAL PROCEDURES

2.1 Crystal Synthesis

TTMZS salt was synthesized by dissolving Thiourea (AR grade), Magnesium Sulphate Hepta Hydrate (AR grade) and Zinc Sulphate Hepta Hydrate (AR grade) in the ratio

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3:0.25:0.75 in double distilled water. The prepared solution was slightly heated and the solvent allowed to evaporate. TTMZS was synthesized as per the following reaction:

$3[CS\ (NH_2)_2] + MgSO_4.7H_2O + ZnSo_4 \rightarrow MgZn[CS\ (NH_2)_2]_3SO_4.7H_2O$

The synthesized TTMZS salt was purified by successive recrystallization process.

2.2 Crystal Growth

In order to grow bulk single crystals of TTMZS, the solubility of the synthesized material was determined at different temperatures ($35-45^{\circ}$ C). The gravimetric method was adopted to determine solubility and this was carried out in a constant temperature bath ($\pm 0.01^{\circ}$ C). The solution was stirred continuously for 6 hours using a magnetic stirrer. The saturated solution prepared at 35° C was filtered using Whatman filter paper. The filtered solution was taken in a beaker and closed with a perforated cover. It was kept in a constant temperature bath maintained at 35° C. The solvent was allowed to evaporate slowly. TTMZS crystals of



Figure 1. TTZMS crystals grown using Solvent Evaporation method.

optimum size were harvested from the mother solution in a time span of 30 days. The TTMZS crystals thus grown are shown below.

3. RESULTS AND DISCUSSION:

3.1 X-Ray Diffraction Analysis

The grown crystals were subjected to Single Crystal X- ray Diffraction using an ENRAF NONIUS CAD-4 diffractometer with Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. The crystal belongs to orthorhombic system. The observed unit cell parameters are given in Table 1 below and the observed values are compared with the reported values of Tris Thiourea Magnesium Sulphate.

Table 1. Indexed Powder XRD Pattern of TTMZS.

| Sl.No | Cell Parameters in Angstrom Units | | Volume ³ in Å | System α=β=γ= 90 | |
|-------|--------------------------------------|-------|--------------------------------|---------------------|--------------|
| | а | b | с | | |
| TTMZS | 15.572 | 6.315 | 5.549 | 545.46 | Orthorhombic |
| TMS | 5.482 | 7.672 | 8.562 | 360 | Orthorhombic |

The Powder XRD pattern of TTMZS was recorded using a Rich Seifert diffractometer with Cu K α ($\lambda = 1.54059$ Å) radiation. The powder sample was scanned over the range of 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed.



Figure 2. X-Ray Diffraction Analysis

3.2 FT-IR analysis

Fourier Tranform Infrared (FT-IR) spectrum was recorded with a Perkin-Elmer RXI spectrometer using KBr pellet technique. The wave number was varied between 400 and 4000 cm⁻¹ in order to confirm the presence of functional groups and the coordination of ligand-to-metal ions. The recorded FT-IR spectrum of the TTMZS compound is shown in figure 3. In the high frequency region sharp intense peaks observed at 3313 and 3192 cm⁻¹ are attributed to asymmetric and symmetric stretching vibrational modes of NH₂ group present in the Thiourea molecule. The NH₂ bending of Thiourea is observed to form a broad envelope between 3300 and 1600 cm⁻¹ due to its Hydrogen bonding interaction with the neighbouring anion complex. The C=S stretching in Thiourea molecule coordinated with Magnesium and Zinc Sulphate is observed at 1508 (asymmetric) and 712 (symmetric) (Table 2).

Besides, this interaction is also evident to be a shift in the N-C-N stretch of Thiourea to higher value in TTMZS crystals compared to pure Thiourea.



In pure Thiourea, C=S is bonded to NH₂, whereas in TTMZS crystals it is bonded to metal ions and therefore the C=S stretching vibration is also shifted to lower values from 730 to 713 cm⁻¹. This shifting of C=S stretching frequency confirms the coordination of metal-sulphur bond. The intense band at 618 cm⁻¹ is due to NH₂ bending vibration. The peak at 1627 cm⁻¹ with very strong intensity can be attributed to the NH₂ asymmetric bending vibrations. The strong band centered at 1122 cm⁻¹ corresponds to NH₂ rocking vibrations. The N-C-N symmetric stretching vibration of pure Thiourea occurs at 1470 cm⁻¹. The strong peak at 1399 cm⁻¹ can be attributed to C=S asymmetric stretching vibration of TTMZS complex. From the FT-IR spectral analysis, the presence of functional groups and the coordination ligand of TTMZS were confirmed and the assignment of functional groups is compared with Tris Thiourea Magnesium Sulphate (MTS) [12] is given in table below.

Table 2. Indexed powder XRD pattern of TTMZS.

| TMS Wave Number -1 (Cm) | TTMZS Wave Number (Cm ⁻¹) | Assignments | | |
|-------------------------------------|--|--|--|--|
| 3368 | 3313 | Symmetric stretching(NH ₂) | | |
| 1611 | 1627 | NH ₂ bending | | |
| 1472 | 1508 | C=S Stretching (Asymmetric) | | |
| 713 | 712 | C=S Stretching(Symmetric) | | |
| 619.04 | 618 | N-C-N Asymmetric stretching | | |
| 955 | 900 | N-C-N symmetric Stretching | | |

UV-Vis Studies

The UV-Vis transmittance spectrum of a TTMZS crystal with 2 mm thickness was recorded using Perkin Elmer-Lambda 35 UV-Vis spectrophotometer in the range of 190-1100 nm. The figure below shows the transmittance spectrum for the entire visible region. The UV transparency lower cutoff wavelength occurs at 280 nm. The absence of absorption of light in the visible region (300-800 nm) makes TTMZS crystals very suitable for optoelectronic applications.



Figure 4. UV-Vis transmittance spectrum of TTMZS

3.3 Thermal Analysis

Thermal analysis was carried out using SDT Q600V 8.3 build 101 simultaneous DTA/TGA analyzer in a nitrogen atmosphere. The Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out for a sample of weight 2.5510 mg in the temperature range 20-1200°C at a heating rate of 20°C/min in nitrogen atmosphere (figures 4 and 5). From TGA it is observed that the crystal TTMZS has good thermal stability up to 248.68°C as there is no weight loss below that temperature.

The TGA curve also shows that there is a weight loss of about 55.3% in the temperature range 300° C-362.88°C due to the liberation of volatile substance in the compound. The DTA curve shows the exothermic peak at 248.75°C – the melting point of the substance – and it undergoes an irreversible endothermic transition thereafter.

The second endothermic peak at 306.78°C indicates major decomposition of the material. The sharpness of the endothermic peak shows a good degree of crystallinity of the grown crystal TTMZS.





Figure 5. TGA Analysis of TTMZS Crystal.

3.4 NLO Analysis

The Second Harmonic Generation (SHG) conversion efficiency of TTMZS was measured by powder Kurtz and Perry Powder Technique [11]. The crystal was ground into a fine powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to strike the sample cell. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube. Powdered Potassium Dihydrogen Phosphate (KDP) was used in the same experiment as a reference material.

3.5 EDAX Analysis

EDAX (Elemental Dispersive X-ray Analysis) is a widely used technique to analyze the chemical components in a material under a scanning electron microscope. This method detects the X-rays produced as the result of the electron beam interactions with the sample. Mapping X-ray data is processed to obtain the percentage of each measured element present in the individual particles. In this communication we have found the accurate proportion of Magnesium and Zinc molecules in the TTMZS complex.



Figure 7. EDAX Analysis of TTMZS Crystal

4. CONCLUSION

Pure TTMZS single crystals of good optical quality have been grown by the Solution Growth method at room temperature. The lattice parameters have been determined by Single Crystal X-ray Diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the absorbance is less than one unit between 300 and 1200 nm. TGA and DTA studies reveal that the TTMZS crystals have good thermal stabilities. The studies on the NLO property confirms the second harmonic conversion efficiency of the crystal to be better than that of KDP.

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COPPER THIN FILM SPUTTERED ON AISI 316L FOR ANTIMICROBIAL PROPERTY

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Abstract: The surgical and other biological instruments are made of Stainless Steel AISI 316L which lacks antimicrobial properties. Copper is coated on Stainless Steel substrate using DC Magnetron sputtering which is used to achieve required film of thickness (0.5-8µm). The deposition pressure, substrate temperature, power supply, distance between the specimen and target are optimized and maintained constant, while the sputtering time (30-110 minutes) is varied. The sputtered copper thin film's morphology, compositional is characterized by SEM and EDAX. X-ray diffraction analysis shows copper oriented on (111) and (002) and copper oxide on (111) planes. The contact angle of copper thin film is 92° while AISI316L shows 73°. The antimicrobial studies carried in *Staphylococcus aureus, Escherichia Coli, Klebsiella pneumonia* and *Candida albicans* shows that CFU/mL was reduced to 30 after 24 hours. The cell viability is studied by MTT assay test on Vero cell line for 24 hours, 48 hours and 72 hours and average cell viability is 43.85%. The copper release from the thin film to the culture medium is 4826µg/L (maximum) is estimated from AAS studies. The bacteria and fungi are found to be destroyed by the copper thin film but do not show much reaction with living Vero cells.

Keywords: Stainless Steel AISI 316L, Direct Current Magnetron sputtering, Copper thin film, Anti-microbial effect, MTT assay

1. INTRODUCTION

Recently many surface coating technologies have emerged to enhance the functional properties like biocompatibility and antimicrobial effect of surgical tools and medical devices. Although various methods have emerged to control the bacterial growth and contamination on medical devices and surgical tools, one of the important and highly successful method for achieving this is by surface engineering technique like thin film deposition on surgical tools to enhance their anti-microbial activity. It is a known fact that stainless steel is one of the mostly employed materials in day-to-day life. However, Stainless steel with added anti-microbial effect increases its influence in medical devices and surgical tools[1]. Even though there are many methods for modifying the surface of the stainless steel devices, sputter deposition of thin films has increased adhesion of copper layer on the metal surface and increased anti-microbial activity[2]. Copper has long been known for its anti-bacterial activity from the 5th and 6th millennia BC. It has long been used by man, since it was available in its native form, without the use of smelting. The spread of antibiotic resistance through selective pressure began and today has made antibiotic-resistant bacteria ubiquitous in hospitals, nursing homes, food processing plants, and animal breeding facilities. This has raised the need for different approaches to keep pathogenic microorganisms at bay. One such alternative is the use of copper surfaces in hygiene-sensitive areas [3]. The AISI316L stainless steel is coated by copper by the process of DC Magnetron Sputtering, and the structural, compositional and anti-microbial effects of the copper coated surface is studied and results are given below and these results are juxtaposed with the results obtained already due to various findings and the property of copper as an hygienic material used in hospital environments and the related topics are discussed.

2. EXPERIMENTAL PROCEDURE:

Sputtering is a PVD (Physical Vapour Deposition) process for depositing thin films, sputtering means ejecting material from a target and depositing it onto a substrate. The target (copper) is the source material. Substrates (stainless steel 316 L) are placed in a

vacuum chamber and are pumped down to a prescribed process pressure. Sputtering starts when a negative charge is applied to the target material causing a plasma or glow discharge. Positive charged gas ions generated in the plasma region are attracted to the negatively biased target plate at a very high speed. This collision creates a momentum transfer and ejects atomic size particles form the target. These particles are deposited as a thin film into the surface of the substrates. Magnetron sputtering is employed because, magnets are used to increase the percentage of electrons that take part in ionization events, increase probability of electrons striking Argon(inert gas inside the chamber), increase electron path length, so the ionization efficiency is increased significantly. Other reasons to use magnets are, Lower voltage needed to strike plasma, Controls uniformity, Increased deposition rate. Once the atoms are sputtered from the copper target, they are accelerated to high potentials in the gap between the electrodes due to applied voltage and they strike on SS 316L substrate at high velocity[1,2,4]. The growth of thin films is influenced by the type of substrate material, angle of incidence of the sputtered atoms and their surface energy. Once they get adsorbed on the SS 316L substrate, they travel continuously by random walk, on the metal surface until their energy is lost completely. Then they get deposited as thin films. This high mobility of adatoms reduces the grain boundary of the developed film because, grain boundary acts as a defect in case of thin films, and their deterioration starts at these grain boundaries. Hence sputtering is advantageous to prevent this from happening. The thickness and morphology of thin films depends upon, Gas pressure, sputtering time and current voltage and power density(see Table 1). The optimised parameters for sputtering: Vacuum base pressure: 1*10⁻⁵ mbar, Deposition pressure: 2*10⁻³ mbar, Substrate temperature: 200°C, Distance between substrate target and substrate: 5 cm, Power supply: 175 W (DC).

Coating Time of Grain size S.No. sputtering thickness (nm)(min) (µm) 1 40 1-2 110-317 2 50 2-3 52-216 3 60 3-4 53-146

 Table 1: Variation of Coating characteristics with time of sputtering

3. MATERIALS CHARACTERISATION

3.1 Morphology studies

Typical structure of the thin film deposited by DC magnetron sputtering is a dense columnar structure. The microstructure obtained is due to the mobility of the adatoms on the surface of substrate during growth. The physical model has been proposed by A. Thornton by his SZM(Structure Zone Model)[5] which shows three typical zones on the thin films. The columnar growth is produced by low diffusion of sputter atoms, mobility of the atoms adsorbed on the substrate surface and the atomic shadow effects, which are produced by varying velocity in growth of columns and various incident angles at which adatoms arrive at the surface of substrate. These zones show a higher degree of binding among columns and at the borders of grains in columns. Initially at low time, there are lot of defects and cracks, voids which are present on the surface and the cross section view also shows the same with less column growth on the substrate, aggregation is also present between the columns. For the deposition time of 60min, there is decrease in voids and cracks and an significant increase in the columnar growth of the thin films and an subsequent increase in the surface area as shown in Figure1.



Figure 1:Scanning Electron Microscopy images of different sputter coated samples showing its morphology (a) 40

3.2 Compositional analysis

The images are taken from Carl Zeiss MA15 / EVO 18 which has Tungsten hairpin filament with Oxford Instruments NanoAnalysis INCA Energy 250 Microanalysis System (EDS) with 130eV INCAx-act Peltier cooled Analytical SDD Detector with PentaFET® Precision having capability of Quantitative, Qualitative, mapping, Point & ID etc. including cobolt standard on pin stub. The characteristic X rays from the samples are analyzed to find the composition of the coating. The sample has pure copper with some amount of oxygen as shown in Figure 2.



which forms Cu2O which is confirmed through HR XRD. The oxidation of copper is very small so this copper oxide formed helps in the antimicrobial property and the coating will last for long time. This copper oxide release into the medium which is measured in the ppm range using AAS.

3.3 X ray diffraction analysis

High Resolution X-Ray diffraction (HRXRD) is done in PANalytical X-Pert Pro MRD Resolution 0.0001° /0.36 arcsec Ge- (220) monochromator Triple axis (Xe) detector Pixel detector. As described above, the sputtered coating forms a columnar growth on the preferred planes. Copper being FCC, the



Atoms after a random walk takes (111) and also (002) next preferred planes as shown in Figure 3. As pure copper is sputtered

on the Stainless steel substrate, it forms oxide as the copper oxide has low Gibbs free energy than that of the pure copper. Only 13.31 atomic percent of oxygen is percent on the surface. The kinetics of the oxide is logarithmic in nature as oxidation is at room temperature. The average crystallite size is 16nm with residual strain of 0.814 % (cauchy contribution: 0.58377 & gaussian contribution: 0.74106)

3.4 Mechanism of Copper's Antimicrobial Activity

Copper surfaces affect bacteria in two sequential steps: the first step is a direct interaction between the surface and the bacterial outer membrane, causing the membrane to rupture. The second is related to the holes in the outer membrane, through which the cell loses vital nutrients and water, causing a general weakening of the cell. The actual activity is exhibited when holes are created in the cell membrane. It is strongly suspected that when a bacterium comes in contact with a copper surface, a short circuiting of the current in the cell membrane can occur. This weakens the membrane and creates holes. This is one way of making holes in membrane. Another is an analogy like rust weakening and making holes in a piece of metal. Now that the cell's outer envelope has been breached, there is an unopposed stream of copper ions entering the cell. This puts several vital processes inside the cell in danger. Copper literally overwhelms the inside of the cell and obstructs cell metabolism. When excess copper binds to these enzymes, their activity grinds to a halt.[6,7]. Figure 4 shows the activity of copper on various microbes.



igure 4: Graph showing the activity of ifferent copper coating thickness against ifferent bacteria and fungus

3.5 MTT Assay

In Vitro assay for Cytotoxicity activity (MTT assay)[8] Cells (1 \times 105/well) were plated in 24-well plates and incubated in 370C with 5% CO2 condition. After the cell reaches the confluence, the samples were added and incubated for 24 hours. After incubation, the sample was removed from the well and washed



with phosphate-buffered saline (pH 7.4) or MEM without serum. 100μ /well (5mg/ml) of 0.5% 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl--tetrazolium bromide (MTT) was added and incubated for 4 hours. After incubation, 1ml of DMSO was added in all the

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wells .The absorbance at 570nm was measured with UV-Spectrophotometer using DMSO as the blank. Measurements were performed and the concentration required for a 50% inhibition (IC50) was determined graphically. The samples are compared and it is shown in Figure 5. The % cell viability is

calculated using Eq. 1:

% cell viability = A570 of treated cells / A570 of control cells \times 100 (1)

3.6 Copper release rate

Sputtered coated samples of different thickness are immersed in a medium containing 90% Dulbecco's Modified Eagle Medium (DMEM) and 10% fetal calf serum in Carbon dioxide atmosphere. The samples for AAS are taken at an interval of 20 minutes, 40 minutes and 60 minutes. After the samples are taken few drops of Conc. Nitric acid is added to make the medium inactive. Copper release from the sputter coated sample was measured using Atomic Absorption Spectrophotometer A700 – Perkin Elmer with Flame [9]. The 50 minute coating shows high release of copper from the surface in 6691 micro gram per liter when the sample is taken after 60 minutes exposure in DMEM. This is parts per billion and very small amount of copper ions are released even after one hour of exposure in DMEM. The release of copper ions for various time in the medium is shown in the Figure 6.



Figure 6 : Copper released from different samples at different time is found using Atomic adsorption spectroscopy

3.7 Polarization Analysis



Figure 7 Tafel Plot of Copper film

The polarization curve for the copper films measured in Simulated Body Fluid solution shows that, as the oxidation time increases, the corrosion potential increases which will reduce the thermodynamics tendency of corrosion as shown in Figure 7. The Tafel plot is plotted with log (i/a) Vs. Potential/V shows a small passivation curve and a large oxide layer curve following the passivation curve.

3.8 Contact angle measurement

The contact angle analysis using the Goniometer yields a value of 73° and 92° (maximum) for substrate and copper coated samples respectively as shown in Figure 8. The columnar structure of the sputtered copper grains increases the contact angle and allows easy cleaning of the sample. The copper film is not hydrophobic in nature but shows a good increase in the contact angle than AISI 316L.



Figure 8 Contact angle measured for (a) AISI 316L and (b) sputter coated copper film sample

4 CONCLUSION

The deposition of Cu thin film coating on AISI316L was done successfully using DC Magnetron sputtering. The structural and compositional analysis of the thin film on the substrate shows a dense columnar structure with increasing density as the sputtering time increases and it mainly contains Copper (86.69%) and a very small amount of Oxygen (13.31%) on the surface and it is also proven by characteristic X-ray analysis, which shows that O₂ which is present, forms Cu₂O shown by HR-XRD (peak along [111]). The anti-microbial property of AISI316L has been greatly improved by the deposition of Cu on its surface. The biocompatibility test (MTT assay) has done on Vero cell line shows 43.85% viability after 72h. The deposited layer was not only stable, but also adherent to the substrate. The modified SS surfaces with its high bacterial killing rate and its durable nature make them promising candidates in hospital environments for surgical instruments and other similar applications.

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Second order and Third order NLO studies of L- alanine crystals grown in aqueous solution of hydrofluoric acid (LAHF)

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Tamil Nadu, India

Abstract: Nonlinear optics is a fascinating field, which plays a vital role in the emerging field of photonics and optoelectronics. A nonlinear optical crystal of L-alanine grown in aqueous solution of hydrofluoric acid is done by slow evaporation method. L-alanine is an NLO material and it has a Second Harmonic Generation (SHG) efficiency of about 0.3 times that of KDP. To alter the various properties of L-alanine, single crystals of L-alanine have been grown in the aqueous solution of hydrofluoric acid. In this work, L-alanine was admixtured with hydrofluoric acid (LAHF) in the molar ratio of 1:1. The grown crystals were colorless and transparent and they were subjected to various studies for characterization. The third-order nonlinearities of LAHF crystal have been investigated by Z-scan method. The values of nonlinear refractive index (n₂), the nonlinear absorption coefficient (β) and third-order nonlinear susceptibility ($\chi^{(3)}$) are estimated for the sample

Keywords: L-alanine; admixtured crystal; solution growth; NLO;XRD; SHG; THG.

1. INTRODUCTION

In recent years, many significant achievements have been made in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic type [1-3]. The need for nonlinear optical materials is much more than other materials because of their significant impact on laser technology, optical communication, optical data storage technology etc [4]. Amino acids are a group of organic compounds containing two functional groups such as amino group and carboxylic group. Most of the amino acids and their complexes belong to the family of organic and semiorganic nonlinear optical (NLO) materials that have potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing. Among the amino acids, L-alanine is the simplest acentric crystal and it is a naturally occurring chiral amino acid with a nonreactive hydrophobic methyl group (CH₃) as a side chain. Lalanine molecule exists as a zwitterion, where the carboxylic group dissociates and the amino group protonates. Efforts have been made on the amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and nonlinear optical properties. If Lalanine is mixed with different organic and inorganic acids to form novel materials, it is expected to get improved NLO properties [5]. Some complexes of L-alanine have been recently crystallized and various studies have been investigated by many researchers [6-9]. Keeping this in mind, L-alanine is mixed with hydrofluoric acid to form L-alanine hydrogen fluoride crystal by slow evaporation method. But the results showed that the expected crystal is in fact Lalanine crystal with the altered properties in comparison that of L-alanine grown in water. For the first time We report here the investigations on the second order and third order NLO studies of L-alanine crystals grown in aqueous solution of hydrofluoric acid.

2. SOLUBILITY AND GROWTH

The salt of L-alanine admixtured with hydrofluoric acid (LAHF) was synthesized by taking L-alanine (99% purity) and analar grade hydrofluoric acid in the molar ratio of 1:1 in double distilled water. The dissolved solution was heated at 50 °C for the synthesis of LAHF salt. The purity of the synthesized salt was further increased by repeated recrystallization. The solubility of the synthesized salt was measured by gravimetrical method [10]. Fig.1 shows the solubility curve for LAHF sample and it is observed that the solubility of LAHF sample in water increases with temperature, exhibiting a positive temperature coefficient of solubility. The saturated solution of the re-crystallized salt of LAHF was prepared in accordance with the solubility data and the calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 2 h using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation method. The harvested crystal of LAHF is shown in the figure 2.

3. SINGLE CRYSTAL XRD ANALYSIS

The structure of the grown LAHF crystal was analyzed by employing a Bruker-Nonious MACH3/CAD4 single crystal X-ray diffractometer. From the single crystal X-ray diffraction data, it is observed that the LAHF crystal belongs to orthorhombic structure with the lattice parameters a = 5.759(2) Å, b = 6.042(4) Å, c=12.358(3) Å, $\alpha = \beta = \gamma = 90^{\circ}$ and V =430.01(1) Å³. The obtained structural data for the grown crystal of this work are almost coincided with those of L-alanine crystal and therefore the crystal structure of LAHF crystal is not changed [11].The slight changes in lattice

parameters may be due to incorporation of admixtured material into the lattice of the crystal.

4. SECOND HARMONIC GENERATION ANALYSIS (SHG)

The NLO activity in reference to SHG of a sample can be checked using the Kurtz and Perry method [12].



Figure 1. Solubility curve of LAHF sample.



Figure 2. Grown crystal of LAHF.

A high intensity Nd:YAG laser ($\lambda = 1064$ nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission.($\lambda = 532$ nm). The second harmonic generation signal of 9.3 mJ for LAHF sample was obtained for an input energy of 0.68 J. But the standard KDP crystal gave an SHG signal of 8.8 mJ for the same input energy. Thus, it is noticed that the SHG efficiency of the grown LAHF sample is 1.05 times that of the standard KDP crystal. It is to be mentioned here that the particle size has been maintained at about 150 microns for both LAHF and KDP samples.

5. THIRD HARMONIC GENERATION ANALYSIS (THG)

Third harmonic generation analysis is done by Z-scan technique. It is a standard technique for determining the nonlinear index of refraction (n_2) and nonlinear absorption coefficient (β) of samples [13,14]. The study of nonlinear refraction by the Z-scan method depends on the position (Z) of the thin sample under the investigation along a focused Gaussian laser beam. The sample causes an additional

focusing and defocusing, depending on whether nonlinear refraction is positive or negative. Measurements of open and closed aperture of the normalized transmittance and sample position Z has a peak to valley shapes are shown in Fig.3 and. The curves are characterized by a prefocal transmittance maximum (peak) followed by a postfocal transmittance minimum (valley) intensity. The transmission difference between peak and valley ($\Delta T_{p\text{-v}}$) is written in terms of phase shift .

$$\Delta T_{p-v=0.406(1-s)} |\Delta \phi|$$

Linear transmittance aperture (S) is calculated using the relation

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right)$$

Where r_a is the radius of the aperture and ω_a is the beam radius at the aperture. The third-order nonlinear refractive index (n_2) of the crystal was calculated by following the relation.

$$n_2 = \frac{\Delta \phi}{KI_0 L_{ef}}$$

Where I_0 is the intensity of the laser beam at the focus (Z = 0) and K = $2\pi/\lambda$ (λ is the wavelength of laser beam).



The effective thickness can be calculated using the relation $I = \frac{1}{2} - \frac{1}{2} -$

$$L_{eff} = 1 - \exp(\alpha L / \alpha)$$

Where α is the linear absorption coefficient and L is the thickness of the sample. The nonlinear absorption coefficient



Figure 4. Z-scan patten for the sample in closed aperture

(\beta) can be calculated using the following relation $\beta \ = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$

Where ΔT is the one peak value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for two photon absorption process. The real and imaginary parts of the third order nonlinear optical succeptibility ($\chi^{(3)}$) are defined as

$$Re \chi^{(3)} (esu) = \frac{10^{-4} (\epsilon_0 (2n_0^2 n^2))}{\pi} (cm/W)$$

Im $\chi^{(3)} (esu) = \frac{10^{-2} (\epsilon_0 (2n_0^2 \lambda \beta))}{4\pi^2} (cm/W)$
 $|\chi^{(3)}| = [(Re \chi(3))^2 + (Im \chi(3))^2]^{\frac{1}{2}}$

Where ' ϵ_0 ' is the vacuum permitivity, ' n_0 ' is the linear refractive index of the sample and c is the velocity of the light in vacuum. The obtained results from the Z-scan measurement for LAHF crystal are

Laser beam wave length (λ) = 632.8 nm

Spot size diameter in front of the aperture $(\omega_a) = 1$ cm

Aperture radius (\mathbf{r}_a) = 4 mm Incident intensity at the focus ($\mathbf{Z} = \mathbf{0}$)= 2 MW/ cm²

Effective thickness (L_{eff}) = 0.987 mm

Nonlinear refractive index $(n_2) = 1.027 \times 10^{-12} \text{ cm}^2/\text{ W}$

Nonlinear absorption coefficient (β) = 0.108×10⁻⁴ c m/W

Real part of the third-order

nonlinear susceptibility Re ($\chi^{(3)}$) = 0.85 ×10⁻¹⁰ esu

Imaginary part of the third- order

nonlinear susceptibility Im ($\chi^{(3)}$) = 4.57 ×10⁻⁷ esu

The third-order nonlinear susceptibility ($\chi^{(3)}$) =6.67 x 10⁻⁴ esu

The calculated values of the third order nonlinear refractive index (n_2) is 1.027×10^{-12} c $m^2/$ W and the positive value of nonlinear refraction reveals the self-focusing nature and nonlinear absorption co-efficient (β) is 0.108×10^{-4} c m / W and it exhibts the two-photon absorption process. The absolute value of ($\chi^{(3)}$) is 6.67 x 10^{-4} esu and this is due to the π -electron cloud movement from the donor to the acceptor of the L-alanine molecule.

6. CONCLUSIONS

Single crystals of LAHF have been grown by slow evaporation solution growth technique and the grown crystals were transparent with a well defined external appearance. The solubility of LAHF crystal is observed to be increasing with increase in temperature. The unit cell parameters for LAHF crystal have been evaluated by single crystal XRD and the structure is confirmed to be orthorhombic. The NLO efficiency of LAHF sample is found to be 1.05 times that of KDP. The values of the third order NLO parameters for the grown sample were determined by Z-scan technique.

7. ACKNOWLEDGEMENT

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Preparation of nano phosphors by Microwave-assisted combustion synthesis

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Abstract: In this review article, we have discussed synthesizing of nano phosphor materials by the Microwave assisted Combustion process. Several literature conclude that efficient synthesis of nano phosphor materials can be achieved only through microwave-assisted combustion method. Also we have discussed about the principle and working process behind the Microwave process. After undergoing literature survey on combustion process we have discussed the preparation process of fuel to oxidizer ratio which plays a major role for obtaining nano powders that are essential in display application.

Key words: Microwave, Combustion process, Nano phosphors, Display application

1. INTRODUCTION

Nowadays, the interest of the scientific community has been devoted to the progress achieved in synthesis, structural characterization, and the physical properties of nanostructures. Due to their peculiar characteristic and size effects, nanocrystals often show some novel physical properties that are different from those of the bulk and that are of great interest both for fundamental studies and for potential technological applications 1–5]. Researchers have undertaken investigations of the influence of particle size on the optical and the electronic properties of nanocrystal materials containing rare-earth oxides [6, 7]. Phosphors are a group of materials that show promising behaviour when synthesized in nano phase. Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices.

Phosphors are high purity inorganic materials that emit light when exposed to various radiations such as photons, electrons and electric field. The host crystal contains controlled levels of impurity ions (activators) which stimulate or enhance luminescence. Most inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators [8, 9]. Rare earth ions-activated nano structured materials have been attracting much interest in the past few years, due to the excellent luminescence and potential applications in luminescent devices and display equipment, such as lighting, field emission display (FED), cathode ray tubes (CRT), and plasma display panels (PDP) [10-15].

Phosphor materials can be prepare various method such as solid state reactions [16-17], co- precipitation methods [18-19], solgel methods [20-23] and spray pyrolysis process [24-

27] emulsion liquid membrane system, hydrothermal method, high energy ball milling method and combustion method. In general, the rare-earth doped phosphors are mainly synthesized by the solid-state reaction at high temperature. However, this method requires a high processing temperature, a long processing tim'e, repeated milling and washing with chemicals. These processes tend to degrade the luminescence property of the particles and yield irregularly shaped particles. Sol-gel method has also been employed to synthesize nanophosphors by many researchers. The as-prepared powders obtained from the sol-gel method have low crystallinity and often require post-treatment at high temperature, which results in severe agglomerations. Combustion synthesis is a promising particle preparation method because it can employ a wide range of precursors for synthesis of a broad spectrum of functional nanoparticles. The use of combustion can avoid hollowness and provide the high temperature environment which is favorable to phosphor synthesis. The flame temperature and particle residence time, which are very important parameters determining particle characteristics, can be easily controlled by varying fuel and oxidizer flow rates. Moreover, the particle size can be controlled by varying precursor solution concentration and multi-component particles can also be obtained by adding different salts into the solution.

Combustion synthesis offers many potential advantages over conventional technique of synthesis, including simple equipment, short processing time, lower energy requirement and higher purity. The initial combustion process used to the conventional furnace as heating system, However this heating method has some inconvenience such as consuming and generating non-homogenous product [28]. Recently a novel technique called 'microwave- assisted combustion synthesis' is used to synthesize oxide materials.

2. MICROWAVE SYNTHESIS:

Microwave energy synthesis of various materials such as ceramics, metals and composites offers several advantages over conventional heating methods. These advantages include unique microstructure and properties, improved product yield, energy savings, reduction in manufacturing cost and synthesis of new materials.

Microwaves are electromagnetic waves with wavelengths from 1 mm to 1 m and corresponding frequencies between 300 MHz and 300 GHz. [0.915 GHz and 2.45 GHz] frequencies are commonly used for microwave heating. These frequencies are chosen for the microwave heating based on two reasons. The first is that they are in one of the industrial, scientific and medical (ISM) radio bands set aside for noncommunication purposes. The second is that the penetration depth of the microwaves is greater for these low frequencies. However, heating is not necessarily increased with decreasing frequency as the internal field (E) can be low depending on the properties of the material. 2.45 GHz is mostly used for household microwave ovens and 0.915 GHz is preferred for industrial/ commercial microwave ovens. Recently, microwave furnaces with variable frequencies from 0.9 to 18 GHz have been developed for material processing (Sutton 1989; Thostenson and Chou 1999). Microwaves are coherent and polarized and can be transmitted, absorbed, or reflected depending on the material type [29].

Microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer. Since microwaves can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating. Hence, it is possible to achieve rapid and uniform heating of thick materials. Therefore, the thermal gradient in the microwave processed material is the reverse of that in the material processed by conventional heating. In conventional heating, slow heating rates are selected to reduce steep thermal gradient leading to process-induced stresses. Thus, there is a balance between processing time and product quality. During microwave processing, the potential exists to reduce processing time and enhance product quality as microwaves can transfer energy throughout the whole volume of the material. In this case, energy transfer occurs at a molecular level that can have some additional advantages. When microwave energy is in contact with materials having different dielectric properties, it will selectively couple with the higher loss tangent material. Therefore, microwaves can be used for the selective heating of the materials. Figure 1 shows a schematic diagram of a typical microwave oven.



Figure 1 shows schematic diagram of a typical microwave oven.

2.1 Microwave-material interaction

Microwave energy is transferred to the material by interaction of the electromagnetic field at the molecular level. The dielectric properties determine the effect of the electromagnetic field on the material. The interaction of microwaves with a dielectric material results in translational motions of free or bound charges and rotation of the dipoles. The resistance of these induced motions due to inertial, elastic, and frictional forces causes losses resulting in volumetric heating

The power absorbed per unit volume, P (W/m^3) is expressed as (Sutton 1989),

$$\mathbf{P} = \sigma |\mathbf{E}|^2 = 2\pi \mathbf{f} \, \varepsilon_0 \varepsilon'_r \, \tan \, \delta |\mathbf{E}|^2, \tag{1}$$

Where E (V/m) is the magnitude of the internal field, σ the total effective conductivity (S/m), f the frequency (GHz), ϵ_0 the permittivity of free space ($\epsilon_0 = 8.86 \times 10{-}12$ F/m), ϵ'_r the relative dielectric constant and tan δ the loss tangent. Equation (1) demonstrates that the power absorbed varies linearly with the frequency, the relative dielectric constant, loss tangent and the square of the electric field. The penetration depth of the microwaves (D) at which the incident power is reduced by one half is expressed as

$$\mathbf{D} = \frac{3\lambda_0}{8.686\pi \tan \delta (\varepsilon_r' / \varepsilon_0)^{1/2}}$$
(2)

where λ_0 is the incident or free-space wavelength The relative dielectric constant and the loss tangent are the parameters that describe the behavior of a dielectric material under the influence of the microwave field. [30].

Microwave synthesis can be used to produce various materials such as, ceramic powders, nanotubes, glasses, micro tubes, metal powder and nanomaterials. Microwave assisted combustion synthesis is one of the approach to produce nano phosphor material.

3. MICROWAVE ASSISTED COMBUSTION SYNTHESIS

Solution combustion is a well-known method for rapid synthesis of rare earth activated insulating materials at low temperatures (350-500°C) and very short times (< 5 minutes). Although oxide phosphors synthesized by a combustion reaction have low-voltage cathodoluminescence efficiencies, hydrothermal, solid-state and combustion methods yield the same efficiencies at excitation voltages below 600 V. Different structures of tricolor phosphors such as oxides, vanadates, borates, aluminates, etc., can be synthesized using a solution combustion method[31].

For the preparation of GdCaAl₃O₇: Eu nanoparticles[32], All the chemicals used were of high purity (Aldrich 99.99%). Stoichiometric amounts of metal nitrates $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Eu(NO_3)_3$ and $Gd(NO_3)_3$ were mixed in minimum doubly distilled water. Then the fuel to oxidizer (F/O) ratio was calculated based on the following Stoichiometric equation.

0.95Gd (NO3)3 + 0.05Eu (NO3)3 + Ca (NO3)2 + 3Al (NO3)3 + 8NH2CH2COOH + 0.5O2→ Gd0.95CaAl3O7: Eu0.05 + 16CO2 + 20H2O + 11N2

The fuel to oxidizer ratio determined by following formula

 $\Phi_{e} = \frac{\sum (\text{coeff.of oxidizing element in specific formula}) \times (\text{valancy })}{-1 \sum (\text{coeff. of reducing element in specific formula}) \times (\text{valency })}$

Stoichiometric proportions of the reactants yield $\Phi_e = 1$, fuellean proportions yield $\Phi_e > 1$, and fuel-rich proportions yield $\Phi_e < 1$ [33]. Then, Stoichiometric amounts of fuel (such as urea, Glysine, hydra zinc, (carbohydrazide) were added. The final solution was converted to a gel by heating up to 80-90 °C. The beaker was transferred into a microwave oven (Samsung, Korea, 900W, 2.45GHz frequency) to complete the combustion reaction. All experiments were performed at a maximum power of microwave for 50 seconds.

The structures of the powders obtained were characterized by X-ray Diffraction (XRD). The morphology of the particles and agglomerates ere also investigated by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The luminescent properties of the powders obtained were characterized using a photoluminescence spectrophotometer. This technique has been applied to successfully synthesize a variety of oxide phosphors, such as GdCaAl₃O₇: Tr [34], Y₂-xO₃:xTb³⁺ [35], these nano phosphors are used to red, green, and blue color emission in plasma display panels.



Figure.2 SEM images of GdCaAl₃O₇: Eu (Ref 32)



Figure.3 SEM images of GdCaAl₃O₇: Tb³⁺ (Ref 34)

4. CONCLUSION

In the past few decades significant developments in the field of microwave assisted combustion process for the preparation of nano phosphor materials have taken place vigorously. In accordance with this process many research works are being conducted to obtain a detailed understanding about the nature and distribution of the electromagnetic field inside the microwave cavity, microwave-material interaction, material transformations and heat transfer mechanisms for optimizing the process. Thus Microwave-assisted combustion synthesis is suitable method for the preparation of nano phosphor materials, since it is a short time process.

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Unimolecular Nanocarriers with pH-Triggered Drug Releasing Properties for Tumor-Targeted Drug Delivery

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Abstract: Unimolecular micelles based on amphiphilic hyperbranched block copolymer, Boltorn[®] H40-poly(L-aspartate-doxorubicin)b-poly(ethylene glycol)/FA-conjugated poly(ethylene glycol) were synthesized as a carrier for tumor-targeted drug delivery. The anticancer drug doxorubicin (DOX) was covalently conjugated onto the hydrophobic segments of the amphiphilic block copolymer arms by pH-sensitive hydrazone linkage. These unimolecular micelles could be a promising nanocarrier with excellent in vivo stability for targeting the drugs to cancer cells and releasing the drug molecules inside the cells by sensing the acidic environment of the endosomal compartments.

Keywords: micelles; drug delivery; targeted; tumor; cytotoxicity

1. INTRODUCTION

Amphiphilic block copolymers have recently attracted much attention in various medical and biological fields since they behave as self-assembled micelles in aqueous solutions [1]. However, the formation of classical multimolecular micelles via self-assembly of linear amphiphilic block copolymers is thermodynamically favorable only above the critical micelle concentration (CMC) of the amphiphilic molecules. When the concentration drops below the CMC, the micellar structure becomes unstable and dissociates into free chains. Such thermodynamic instability of the micelles below the CMC is a major concern for their in vivo drug delivery application [2]. To overcome this problem, in this work, we report the synthesis and characterization of folate (FA)-conjugated unimolecular nanocarriers based on a hyperbranched polymer (H40) core, a hydrophobic poly(L-aspartate-doxorubicin) inner arm, and a hydrophilic poly(ethylene glycol) and FAconjugated poly(ethylene glycol) outer arm as a tumortargeted drug delivery carrier. The anticancer drug, DOX, was conjugated to the hydrophobic inner arm of the polymer by pH-sensitive hydrazone linkage. Conjugation of DOX to the polymeric core is expected to improve the drug loading level and to reduce the chance of premature drug release outside the tumor cells. Moreover, FA-conjugated nanocarriers can be directed to the cancer cells and subsequently internalized in the target cell via receptor-mediated endocytosis [3]. Since hydrazone linkage between the DOX and polymer is prone to hydrolysis in acidic condition, the release of DOX from the micelles will be facilitated in the acidic environment of the endosomal compartments after the nanocarriers are internalized by the tumor cells [4].

2. EXPERIMENTAL METHODS

Unimolecular nanocarrier was prepared using three-step reaction procedure. First, $poly(\beta$ -benzyl L-aspartate)-*b*-PEG copolymer was prepared by ROP of β -benzyl L-aspartate N-carboxyanhydride using HO-PEG-NH₂ as an initiator. Thereafter, the formed product was conjugated with the carboxyl terminal groups of H40-COOH to obtain the nanocarriers with OH end groups. In the last step, FA was conjugated on the surface of the nanocarriers in presence of DCC and DMAP in anhydrous DMF to obtain FA-conjugated nanocarriers. This product was then conjugated with DOX using hydrazine (see Figure 1).

The unimolecular micelles were prepared using the membrane dialysis method. Briefly, the DOX conjugated polymer (50

mg) was dissolved in 5 mL of DMF under stirring. With this solution, 15 ml of deionized water was added dropwise. Thereafter, the polymer solution was dialyzed against Millipore water using a cellulose dialysis tubing (Molecular weight cut-off, 2 kDa) for 96 h. The properties of the nanocarriers were determined by DLS and TEM analyses.

The *in vitro* release studies were performed at pH 5.3, 6.6 and 7.4 at 37 °C. Briefly, 50 mg of micelles was dispersed in 5 ml of medium and placed in a dialysis bag with a molecular weight cut-off of 2 kDa. The dialysis bag was then immersed in 95 ml of the release medium and kept in a horizontal laboratory shaker maintaining a constant temperature and stirring. Samples (2 ml) were periodically removed and the volume of each sample was replaced by the same volume of fresh medium. The amount of released DOX was analyzed with a spectrophotometer at 485 nm.

The cellular uptake and cytotoxicity of the nanocarriers against 4T1 mouse mammary carcinoma cells was assessed using flow cytometry and MTT assay, respectively using the standard protocol.



Figure 1. Synthesis of unimolecular nanocarrier.

3. RESULTS AND DISCUSSION

3.1 Micellar properties

Amphiphilic hyperbranched block copolymer, Boltorn[®] H40glycol)/FApoly(L-aspartate-doxorubicin)-b-poly(ethylene conjugated poly(ethylene glycol) formed unimolecular micelles in aqueous solutions because of its amphiphilicity and globular architecture. The size of the micelles was investigated by DLS and TEM. DLS showed a bimodal distribution with a smaller nanocarrier diameter in the range of 17-36 nm and a large micelle diameter in the range of 52-76 nm. The average hydrodynamic diameter was 50 nm with a PDI of 0.122. The broad polydispersity index for the micelles indicated the existence of secondary aggregation [5,6]. Therefore, the smaller micelles in the diameter range of 17-36 nm may be attributed to individual unimolecular micelles. The large size of polymeric micelles with approximately 52-76 nm is most probably due to the formation of secondary aggregates that are clusters of individual unimolecular micelles. TEM showed that the morphology of the unimolecular nanocarriers appeared as bright spheres surrounded by a cloudy ring, and had a diameter in the range of 10-20 nm as shown in Figure 2. The diameter of the unimolecular micelles observed by TEM is smaller than its diameter obtained from the DLS experiment. The diameter of the micelles obtained from the DLS experiment reflects the hydrodynamic diameter of the micelles, whereas the diameter of the micelles observed by TEM shows that of dried micelles. Therefore, an increase in the micelle size obtained from DLS compared with that of TEM is assumed to be caused by the hydration of the shell



Figure 2. TEM image of unimolecular micelles.

3.2 In vitro drug release properties

In vitro drug release study showed that the pH of the medium had a strong effect on the DOX release rate from the micelles. The drug release at pH 7.4 was considerably slow, with an initial burst of about 7%, and only 15% of the drug released after 45 h. This result suggests that unimolecular micelles maintained drug-polymer interactions by the hydrazone linkage under physiological conditions (see Figure 3). At pH 5.3 and 6.6 the DOX release rate was much faster, with approximately 90 and 83% of the drug released within 45 h, respectively. This result shows that the release of DOX from the micelles in an acidic environment was governed by the acid-cleavable characteristic of the hydrazone linkage between the DOX molecules and the polymer backbone. An acid-cleavable hydrazone linkage can undergo hydrolysis under acidic conditions; thus, unmodified DOX can be released from the micelles by hydrolysis of the hydrazone linkage between the micelles and DOX molecules.



Figure 3. DOX release profile from the micelles.

The pH-dependent releasing behavior is of particular interest in achieving tumor-targeted DOX delivery with micelles. It is expected that most DOX conjugated with micelles will remain in the micelle cores for a considerable time period when the injected micelles stay in the plasma at normal physiological conditions (pH 7.4), thereby greatly reducing the side effects to the normal tissues. However, a faster release occurs once the micelles are taken up by the tumor cells via a folatereceptor-mediated endocytosis process because the pH values of the endocytic compartments ranges from 4.5 to 6.5, which are much lower than the pH value of the normal physiological conditions [7,8]. Therefore, a sufficiently high concentration of DOX can be generated within a reasonably short period of time once the unimolecular micelles are taken up by the tumor cell via folate-receptor-mediated endocytosis, thereby greatly improving the efficacy of targeted cancer therapy.

3.3 Cellular uptake

Flow cytometry analysis was performed to compare endocytosis of micelles with that of FA-free micelles and free DOX using a folate receptor positive cancer cell line, 4T1, in the FA-free incubation medium. Since DOX itself is fluorescent, it was used directly to measure cellular uptake without additional markers. Therefore, the fluorescence intensity is proportional to the amount of DOX internalized by the cells. Flow cytometry histograms of cell-associated DOX fluorescence for 4T1 cells are shown in Figure 4. Cells without any DOX treatment were used as a negative control and showed only the auto-fluorescence of the cells. For 4T1 cells with equivalent DOX concentration in each formulation and same incubation time, the FA conjugated micelles showed higher fluorescence intensity than FA-free micelles. After 15 min of incubation, the amount of cellular uptake of FA conjugated micelles was approximately three times higher than that of FA free micelles. Although uptake of both type of micelles increased after 2 h of incubation, the FA conjugated micelles still showed a four-fold increase in cellular uptake than that of FA free micelles. This result directly confirms that the cellular uptake of the micelles can be enhanced by attaching FA on their surface and the FA conjugated micelles were transported within cells by a folate-receptor-mediated endocytosis process.



Figure 4. Flow cytometry results of 4T1 cells.

3.4 MTT assay

The cytotoxic effects of unimolecular micelles against cultured 4T1 cells were studied using the MTT assay. Figure 5 shows the cytotoxic effect of free DOX, FA conjugated and FA-free micelles against 4T1 cancer cells. As shown in Figure 5, the cell viability in the presence of FA conjugated micelles was lower than that in the presence of FA free micelles. This result reveals that FA moieties in the micelles played an important role in enhancing cytotoxic effect by binding of unimolecular nanocarriers with FA receptors on 4T1 cells, and subsequently increasing their intracellular uptake as a result of the receptor-mediated endocytosis. In the presence of free DOX, the cell viability of the cultured 4T1 cells dramatically decreased, indicating that the cytotoxicity of free DOX was much higher than that of the DOX-conjugated micelles. The cytotoxicity of free DOX was much higher than that of the DOX conjugated micelles. Since DOX is a small molecule, it can diffuse into the cells quickly; however, the DOX conjugated micelles can be internalized in the cells only by the endocytosis process.



Figure 5. Cytotoxicity of free DOX and micelles against 4T1 cells.

4. CONCLUSIONS

Unimolecular nanocarriers conjugated with DOX were prepared for tumor-targeted drug delivery. DLS studies reveled that micelles had a bimodal distribution with a diameter in the range of 17-36 and 52-76 nm. The diameter of the micelles based on TEM was in the range of 10-20 nm. The rate and amount of DOX released from the nanocarriers was higher at acidic medium due to their pH-sensitive hydrazone linkage with the DOX. MTT assay indicated 4T1 cell growth inhibitory activity of the nanocarriers was enhanced due to enhanced cellular uptake. Consequently, it is concluded that the FA-conjugated unimolecular nanocarrier is an excellent nanocarrier for actively delivering drugs inside the tumor cell via folate-receptor-mediated endocytosis. The unimolecular nanocarriers could be a suitable candidate for anti-cancer drug delivery applications due to their small size, pH-triggered drug release properties and active cancer targeting ability.

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Effect of Hippuric Acid on the Growth, Structural and Optical Properties of Non Linear Optical Crystals

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Abstract: Non-linear optical potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) single crystals with 1 mol% of hippuric acid dopant were grown from aqueous solution by employing slow evaporation technique. With appropriate dopants, the KDP and ADP crystals exhibit several desirable properties. Crystallinity of the grown crystals was studied by powder XRD analysis. The bonding structure and molecular associations were analyzed by FTIR spectroscopy. It also confirms the functional groups present in the grown crystals. UV-Vis-NIR spectral analysis was carried out to study the optical characteristics of the crystals which reveal that the cutoff wavelength for both hippuric acid doped KDP and ADP crystals is around 300 nm. Second harmonic generation (SHG) test adopting the Kurtz Perry technique revealed that the SHG efficiency has increased due to doping when compared with pure KDP and ADP crystals.

Keywords: solution growth, single crystals, Powder XRD, UV-Vis-NIR, FTIR, Powder SHG test, optical property.

1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) are promising materials that play an important role in piezoelectric, ferroelectric, electrooptic and nonlinear optical industries. This material attracts the many researchers probably because of their simple structure and many desirable properties associated with a hydrogen bond system involving a large isotopic effect, broad transparency range, high laser damage threshold and relatively low production cost [1, 2].

Nonlinear optics (NLO) has wide applications in the field of telecommunication and information devices [3-7]. Nonlinear optics gives much importance in photonics and optoelectronics technologies. New nonlinear optical frequency conversion materials have a significant impact on laser technology, optical communication and optical data storage [8-10]. Recent interest in quantum electronics has focused on

finding new materials for efficient second harmonic electro optic modulation [11].

The organic doping material contains an optically active atom i.e. it will have hyper polar molecule, which favors the formation of big size crystals [12]. Hippuric acid (HA) with molecular formula C_6H_5 -CO-NH-CH₂-COOH is also referred as benzamino acetic acid is an organic nonlinear material. The molecular and chemical structure of HA are shown in the Figure 1 (a) and Figure 1 (b) respectively. It is formed in the order of orthorhombic structure. It is an excellent material for second harmonic generation because of its high conversion efficiency [13].

The organic NLO materials are sufficiently good over the inorganic materials because they have high nonlinear response. Organic materials are often formed by weak Van der waals force and hydrogen bonds and hence possess high degree of delocalization. The amino acids are the famous organic materials which play a vital role in the field of nonlinear optical crystal growth. Many members of natural amino acids are individually exhibiting the nonlinear optical properties because they have a donor NH_2 and acceptor COOH group and the intermolecular charge transfer is also possible [14]. Since hippuric acid exhibits good nonlinear optical properties, it is of interest to dope it in KDP and ADP crystals. In this work we have investigated the effect of organic dopant in Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) in order to increase the NLO efficiency.

2. SINGLE CRYSTAL GROWTH

Single crystals of 1 mole% hippuric acid doped KDP and ADP crystals were grown by solution growth employing slow evaporation technique. The starting materials were subjected to repeated recrystallization to improve their quality. HA salt was added to the powdered crystalline samples of KDP and ADP in 1 mole% separately to form saturated solutions. The solutions were thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The beakers containing the solutions were closed with perforated cover and kept in a dust free atmosphere. Transparent colorless single crystals with the dimensions 35 mm x 8 mm x 4 mm for HAKDP and 54 mm x 20 mm x 11 mm for HAADP were harvested within 3-4 weeks. The photographs of HAKDP and HAADP crystals are shown in Figure 1 (a), (b)



Figure 1 (a) Single crystal of HA doped KDP



Figure 1 (b) Single crystal of HA doped ADP

3. RESULT AND DISCUSSION

3.1. Powder XRD analysis

Powder X-ray diffraction analysis was performed to confirm the quality of the grown crystals and to identify the cell dimensions using Rigaku X-ray diffractometer with CuK_{α} radiations (λ =1.540 Å) within the 2 θ range 20° - 75°. The powder XRD pattern of HAADP and HAKDP crystals are shown in Figure 2 (a) and 2 (b). Using XRDA the lattice parameter values of grown crystals were calculated as a, b = 7.4993 Å, c = 7.5525 Å for HAADP single crystals and it belongs to tetragonal crystal structure. For HAKDP a=10.5058 Å, b=10.4495 Å, c=6.9186 Å and the crystal system belongs to Orthorhombic. The incorporation of impurity (hippuric acid) in the crystals gives a slight variation in the lattice parameters and the cell volume for the doped crystal naturally varies. It is evident for the incorporation of the dopant, unit cell volume gets increased.



Figure 2 (a) Powder XRD spectrum of HAADP crystal



Figure 2 (b) Powder XRD spectrum of HAKDP crystal

3.2. UV-VIS-NIR optical analysis

The optical properties of the material are important, as they provide information on the electronic band structure, localized state and the type of optical transitions because the absorption of UV and visible light involves promotion of the electron in σ and π orbital from the ground state to higher energy states [15]. The UV-Vis- NIR absorption and transmittance

spectrum was recorded using Jasco V-570 UV-Vis-NIR spectrophotometer. From both the spectrum figure 3 (a), (b), it is found that the cut off wavelength of the hippuric acid doped KDP and ADP crystals is around 300 nm. It is found that there is an absence of absorption in the region between 340 nm and 1200 nm, which are the most desirable properties of the material for NLO application.



Figure 3 (a) Absorbance curve of HA doped KDP



Figure 3 (b) Absorbance curve of HAKDP

3.3. FTIR Analysis

FTIR spectroscopy is effectively used to identify the functional groups in order to determine the molecular structure of the compounds. The FTIR spectrum was recorded by Shimadzu FTIR-8400S spectrometer technique in the range from 400 cm⁻¹ to 4000 cm⁻¹.



Figure 4 (a) FTIR spectrum of HAADP crystal

Figure 4 shows the FTIR spectrums of HAADP single crystal. FTIR spectra of both HAKDP and HAADP confirm the presence of functional groups in the grown crystals.



Figure 4(b) FTIR spectrum of HAADP crystal

3.4. Powder SHG test

Powder SHG test by the Kurtz-Perry technique was adopted for the initial testing of the grown crystals for frequency conversion applications. The fundamental beam of wavelength 1064 nm from a Q-switched Nd:YAG laser was used to test the second harmonic generation property of the grown HAADP and HAKDP crystals. Both the crystals were ground into fine powders and packed in micro tubes mounted in the path of laser pulses operating with a pulse width of 6 ns and a repetition rate 10 Hz and having an input energy of 0.68 ms/pulse. The second harmonic generation of the crystals was confirmed by a green emission with the of wavelength 532 nm from the samples. The second harmonic generation efficiency of 1 mol% HA doped ADP and KDP crystals were found to be 1.5 and 1.2 times that of pure ADP and KDP crystals respectively.

4. CONCLUSION

Good quality of single crystals of hippuric (HA) acid doped KDP (HAKDP) and ADP (HAADP) were grown by solution growth technique for the first time. The structural characterization of the grown crystals was carried out by powder X-ray diffraction studies. UV-VIS-NIR optical analysis shows good optical transmittance in the entire visible region for the above mentioned crystal, also it is found that the UV cut off wavelength is around 300 nm and it can be used as a potential material for SHG in the visible region down to blue and violet lights, which makes it suitable for laser frequency doubling and related optoelectronic applications. The FTIR study confirms the presence of hippuric acid in the grown crystal

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