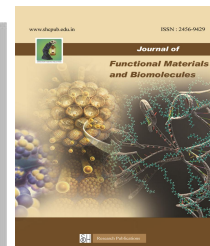




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Structural and Optical characterization of Pure and Cadmium doped Serine Zinc Acetate NLO crystals

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Abstract

Optical quality single crystals of Serine Zinc Acetate (SZA) and Cadmium doped Serine zinc acetate were grown by slow evaporation solution growth technique. The cell dimensions were obtained by single crystal X-ray diffraction study and the results of both SZA and Cadmium doped SZA were compared. The various functional groups were identified from FTIR studies, it showed a little violation between pure and metal doped SZA. The optical behaviour of the grown crystals was analysed through UV-VIS-NIR spectral analyses and gave the transparency range in the visible region. The Vickers microhardness study revealed the hardening nature of the grown materials and it indicates the metal doped SZA had little improved hardness compared to pure SZA. The thermal studies of the pure and cadmium doped SZA crystal indicate a marginal increase in the thermal stability of the doped crystal. The NLO activity of the grown crystals was tested by using Kurtz-Perry powder technique.

Keywords: Single crystal XRD, FTIR, UV-VIS-NIR, Microhardness, Thermal, NLO

1. Introduction

Nonlinear optical organometallic complexes are given much attention because of their ability to combine the flexibility of organic materials with the thermal stability and mechanical strength of inorganic materials [1]. Many amino acids individually exhibit the nonlinear optical properties [2] because they have a donor NH₂ and

acceptor COOH and non-centrosymmetric space group and chiral carbon atom [3]. In this amino acid family Serine is an organic amino acid and exists in a zwitterionic form, which shows a good nonlinear effect [4]. Some of Serine based crystals are Serine sodium nitrate [5], Serine formate [6], and Serine acetate [7], and they have been reported in recent years. In this series, we report the comparative study of synthesis, growth, and XRD, FTIR, optical transmission, micro hardness, TG-DTA and NLO characterization of pure and Cd doped SZA single crystals.

2. Materials and Methods

The commercially available serine and zinc acetate (AR grade) salts are taken in equal molar ratio have been used to synthesize the SZA single crystals. All the preparation and growth process have been carried out in deionized water solution. First zinc acetate was dissolved in deionized water. Serine was then added to the solution slowly by continuous stirring for one hour to form a homogeneous mixture. The final product is filtered by Whatman filter paper and kept in a beaker. The solution was placed in undisturbed position. Within ten days, colorless, optically good quality single crystal of dimension of 3x3x1mm³ was obtained by slow evaporation technique. Cd²⁺ doped SZA crystals were also grown by adopting the same procedure by replacing Zn²⁺ ions in SZA. In a period of 20 days Cd²⁺ doped SZA crystals of dimension of 6x4x2mm³ is obtained. The photograph of

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pure and Cd²⁺ doped SZA were shown in figure 1&2.

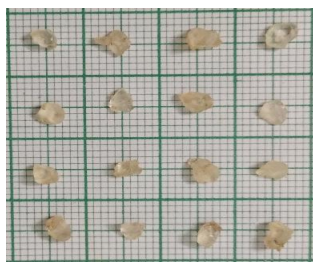


Fig.1. Grown crystal of SZA

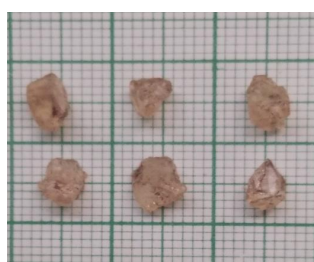


Fig.2. Grown crystal of Cd²⁺ doped SZA

3. Result and Discussion

3.1. Powder XRD studies

The powders X ray diffraction analysis of grown crystals were carried out using the ENRAF NONIUS CAD4 automatic X-ray diffractometer. The collected lattice parameters and cell volumes of the pure and Cd²⁺ doped SZA are presented in Table 1. From the X-ray diffraction data that both the pure and Cd²⁺ doped SZA belongs to orthorhombic system and slight variations in the lattice parameters and cell volume values. These variations may be attributed to the incorporation of Cd²⁺ ions in SZA crystal lattice.

	a (Å)	b(Å)	c(Å)	V (Å ³)
Pure SZA	5.532	9.52	8.421	434.52
Cd doped SZA	5.521	9.65	8.398	435.37

3.2. FTIR Analysis

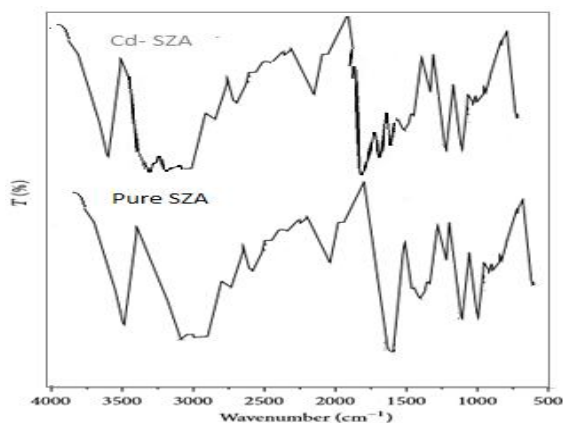


Fig.3. FTIR Spectrum of SZA

The Fourier Transform Infrared spectrum of the grown crystals was recorded in the region of 450-4000 cm⁻¹ using Bruker IFS 66V model by KBr pellet technique.

The characteristic peaks observed in the FTIR spectrum of pure and Cd²⁺ doped SZA are shown in figure 3.

The Serine molecule is more basic and therefore the presence of NH₂ group is revealed in the FTIR spectrum that shows an intense band with strong absorption around 3310 cm⁻¹ and protonated by the carboxyl group (COOH), giving hydrogen bonding interaction between NH₂⁺ and COO⁻. The broad envelop band around 3000 cm⁻¹ to 2000 cm⁻¹ is due to superimposed O-H and NH₃⁺ stretching vibrations. The absorption peak at 1665 cm⁻¹ corresponds to C=O stretching mode. The absorption peak between 930 cm⁻¹ and 1152 cm⁻¹ was assigned to asymmetric coupled vibration of acetate and serine. Comparing the bands, FTIR spectra of pure and Cd²⁺ doped SZA crystals are same with some variations. The peaks around 1700 cm⁻¹ are due to metal linkage with the SZA crystal. So, the FTIR studies qualitatively establish the presence of dopants in the lattice of pure SZA crystals.

3.3. UV-VIS Optical studies

The optical transmission spectra of the pure and Cd²⁺ doped SZA grown crystals were recorded from Lambda-35 spectrometer in the wavelength range of 200nm to 1100nm. Samples of 2mm thickness is used for the transmission data collection. UV-VIS spectrum occurs due to the electronic transitions of the molecules in the compound. The recorded spectra of grown samples were shown in figure 4.

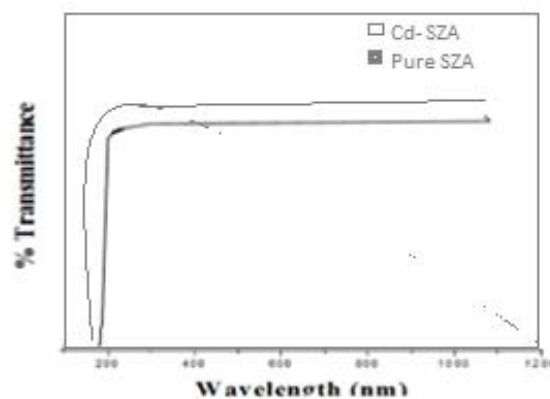


Fig.4. Transmittance graph for SZA

The crystal had a good optical transmission in the entire visible region and the lower cut-off wavelength is

around 245 nm and 232 nm, which confirmed the absence of any overtones and absorbance due to electronic transitions. A graph of percentage of transmission versus wavelength is shown in figure 4. This makes the pure and Cd²⁺ doped SZA crystals were suitable for UV tunable laser and SHG device applications [8].

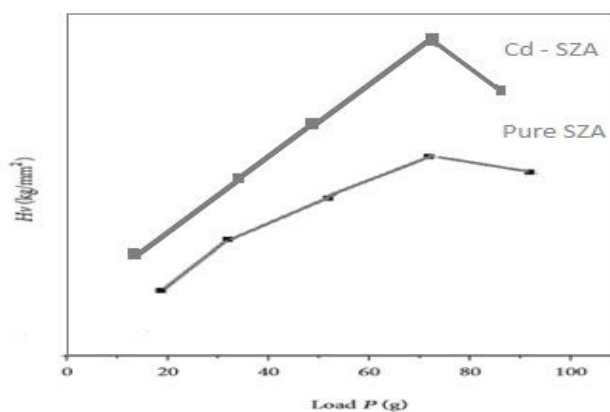


Fig.5. Vicker's Microhardness plot of SZA

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3.4. Microhardness studies

Micro hardness test is the suitable method to find the mechanical property of the materials [9]. The hardness of grown crystal has been evaluated using Vickers's microhardness tester. To evaluate the hardness of grown crystal, smooth surface of the crystal was selected and then subjected to static indentation period of 5s. The indented impressions were approximately square. The microhardness number *HV* is calculated using the relation,

$$HV = 1.855P/d^2 \text{ ----- (1)}$$

Where *P* is the indenter in Kg and *d* is the diagonal length of the impression in mm. From the figure 5 the variation of microhardness number (*Hv*) with applied load is shown. From the graph, the hardness number increases with the increase in load up to 70g for pure SZA and 80g for Cd²⁺ doped SZA crystals respectively. From the result, it is observed that the hardness of Cd²⁺ doped SZA crystals increased than the pure SZA crystals. The addition of Cd²⁺ to SZA probably enhances the strength of the pure material.

3.5. Thermal Analysis

The TG/ DTA analysis of pure and Cd²⁺ doped SZA crystals were obtained by using the instrument TGA Q500 TA. The TGA was carried out in nitrogen atmosphere at a heating rate of 20°C per minute in the temperature range of 30°C to 600°C.

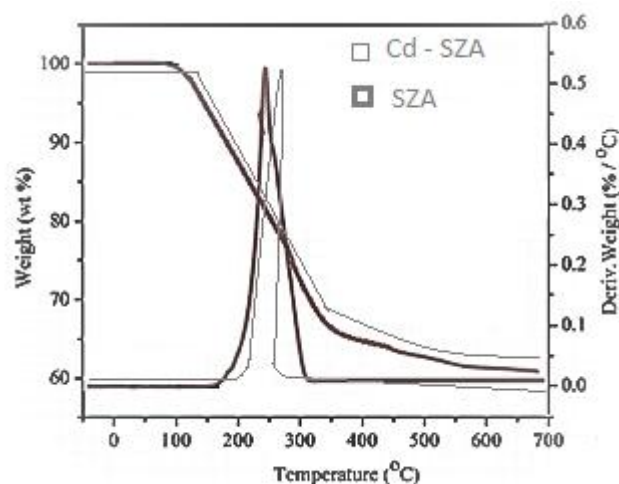


Fig.6. TG-DTA Analysis of SZA

Figure 6 illustrates the TG/DTA curves for both pure and Cd²⁺ doped SZA samples. TGA curve shows that the material is stable up to 115°C and 150°C for pure and Cd²⁺ doped SZA crystals respectively. In DTA curve, the peak at 255°C and 275°C, indicates the melting point of the grown samples. The melting point of serine is 228°C but the endothermic peak observed at 255°C for addition of zinc acetate and 275°C for doping of Cd²⁺ ions. Thus the TG/DTA studies revealed that metal doped crystals are found to be thermally more stable than pure crystals.

3.5. SHG Efficiency test

The grown crystals were powdered and NLO efficiency of the crystal was estimated by using Kurts and Perry technique. The fundamental beam of Q-switched, mode locked Nd: YAG laser operating at 1.06nm and generating pulses of duration 35 ns and 10 Hz repetition. The well-known NLO crystal standard KDP are taken as the reference material and the conversion efficiency of pure and Cd²⁺ doped SZA are 1.1 and 1.8 times. The presence of Cd²⁺ ions in the crystal lattice, there is an increase in polarizability of the molecule, which tends to increase the Second Harmonic generation efficiency.

4. Conclusion

A satisfactory quality single crystal of pure and Cd²⁺ doped Serine zinc acetate (SZA) were successfully grown by using the slow evaporation technique. The cell structure of the crystal confirmed by the single crystal X-ray diffraction analysis and crystallize in orthorhombic system. Optical absorption spectra revealed that the pure and metal doped SZA have a cut-off wavelength at UV region and had low percentage of absorption. The various functional groups have been identified from FTIR spectral analysis. The TG/TDA analysis indicates that the presence of metal dopant (Cd²⁺) slightly increases the decomposition temperature of the SZA. The hardness tests showed that the mechanical strength of Cd²⁺ doped SZA crystal was more than that of pure SZA. The Kurtz powder test proved that the Cd²⁺ metals have increased the efficiency of the SZA crystals by approximately 0.7%. Based on these

observations both the pure and Cd²⁺-doped SZA used for the fabrication of photon devices.

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