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Synthesis, Growth, Structural and Optical characterization of Cadmium doped Serine zinc acetate Non-linear Optical Material

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Abstract

Optical quality single crystals of Cadmium doped Serine zinc acetate were grown, to improve the optical properties. The cell dimensions were obtained by single crystal X-ray diffraction study. The various functional groups were identified from FTIR studies, it showed a little violation in pure SZA. The UV-VIS-NIR spectral analyses gave the transparency range of the grown crystal in the entire visible region. The Vickers microhardness study and TG/DTA studies indicates that the cadmium doped SZA had little improvement to pure SZA. The NLO activity of the grown materials were tested by using Kurtz-Perry powder technique.

Keywords: Single crystal XRD, FTIR, UV-VIS-NIR, 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 NH_2 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 zwitter ionic 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 single crystal XRD, FTIR, optical transmission using UV-VIS-NIR, micro hardness, TG-DTA and NLO characterization of pure and Cd^{2+} doped SZA materials.

2 Experimental

The commercially available Serine and Zinc acetate (AR grade) salts are taken in equal molar ratio have been used to synthesis 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, colourless, optically good quality single crystal of dimension of 3x3x1mm^3 was obtained by slow evaporation technique. Cd^{2+} doped SZA crystals were also grown by adopting the same procedure by adding Cd metal powder after formation of the homogeneous mixture of SZA. In a period of 20 days Cd^{2+} doped SZA crystals of dimension of 6x4x2mm^3 is obtained. The photograph of pure and Cd^{2+} doped SZA were shown in Fig. 1 and Fig. 2.

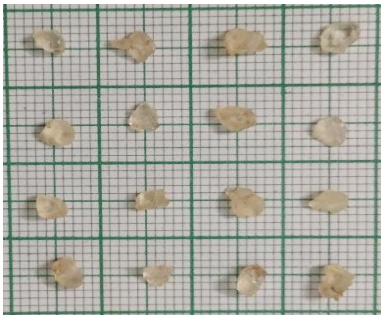

Fig. 1. Grown crystal of SZA

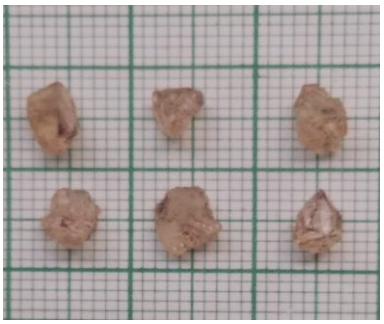

Fig. 2. Grown crystal of Cd^{2+} doped SZA

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3 Results and Discussion

3.1. Single Crystal XRD Studies

The single crystal 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 Cd^{2+} doped SZA are presented in Table 1. From the X-ray diffraction data shows that both the pure and Cd^{2+} 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 Cd^{2+} ions in SZA crystal lattice.

Table 1 Crystal data of pure and Cd^{2+} doped SZA

	Pure SZA	Cd^{2+} doped SZA
a (Å)	5.532	5.521
b(Å)	9.52	9.65
c(Å)	8.421	8.398
V(Å)^3	434.52	435.37

3.2. FTIR Analysis

The Fourier Transform Infrared spectrum of the pure and cadmium doped SZA crystals were 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 Cd^{2+} doped SZA are shown in Fig. 3.

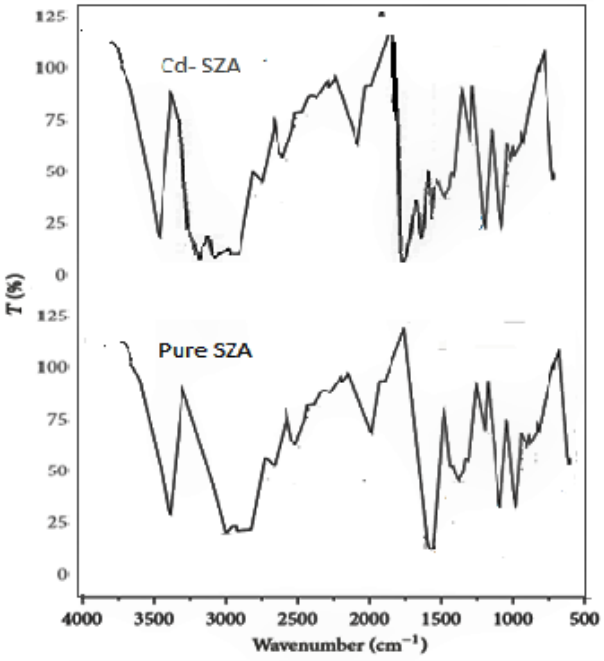

Fig. 3. FTIR Spectrum of pure and Cd^{2+} doped SZA

The Serine molecule is more basic and therefore the presence of NH_2 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 NH_2^+ and COO^-. The broad envelop band around 3000 cm^{-1} to 2000 cm^{-1} is due to super imposed O-H and NH_3^+ 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 Cd^{2+} doped SZA crystals are same with some variations. The peaks around 1700 cm^{-1} is due to metal linkage with the SZA crystal. So, the FTIR studies qualitatively establish the presence of dopants in the lattice of pure SZA materials.

3.3. UV-VIS -NIR Spectral Studies

The optical transmission spectra of the pure and Cd^{2+} doped SZA materials were recorded from Lambda-35 spectrometer in the wavelength range of 200 nm to 1100 nm. Samples of 2mm thickness is used for the transmission data collection. UV-VIS –NIR spectrum occurs due to the electronic transitions of the molecules.

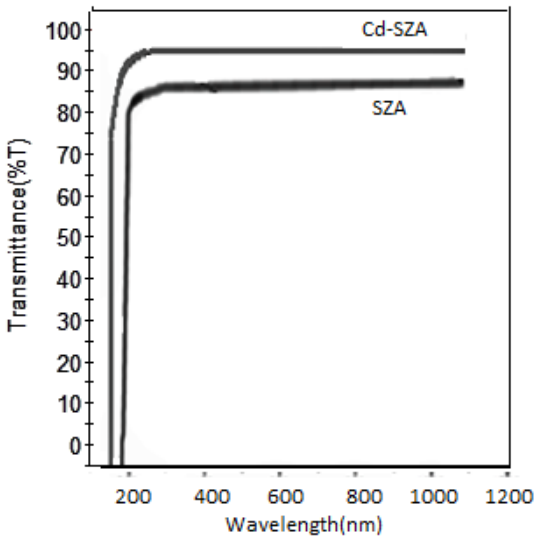

Fig. 4. Transmittance for pure and Cd^{2+} doped SZA

The crystal had a good optical transmission in the entire visible region and the lower cut-off wavelength was 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 Fig. 4. This makes the pure and Cd^{2+} doped SZA materials were suitable for UV tuneable laser and SHG device applications [8].

3.4. Microhardness Studies

Microhardness test was the suitable method to find the mechanical property of the materials. The hardness of grown crystal has been evaluated using Vickers's micro hardness 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 micro hardness number H_V is calculated using the relation,

$$H_V = 1.855p/d^2$$

where, P is the indenter load in g and d is the diagonal length of the impression in mm. From the Fig.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 Cd^{2+} doped SZA crystals respectively.

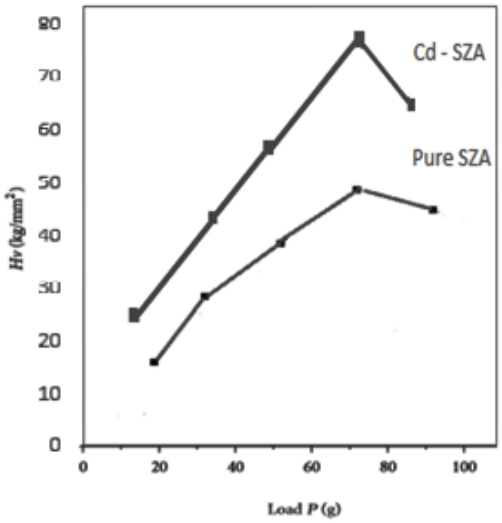

Fig. 5. Microhardness plot of SZA and Cd^{2+} doped SZA

From the result, it is observed that the Cd^{2+} doped SZA crystals had increased hardness value than the pure SZA crystals. The relation connecting the applied load and diagonal length of the indentor is given by Meyer's formula,

$$P = ad^n$$

where, n is the Meyer's index or work harding coefficient. According to Onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft materials [9]. The addition of Cd^{2+} to SZA probably enhance the mechanical strength of the pure material and hence both are belonging to hard material category.

3.5. Thermal Analysis

The TG/ DTA analysis of pure and Cd^{2+} doped SZA materials 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 illustrates the TG/DTA curves for both pure and Cd^{2+} doped SZA samples.

TGA curve shows that the material is stable up to 115˚C and 150˚C for pure and Cd^{2+} doped SZA materials 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 Cd^{2+} ions. Thus, the TG/DTA analysis revealed that metal doped materials are found to be thermally more stable than pure crystals.

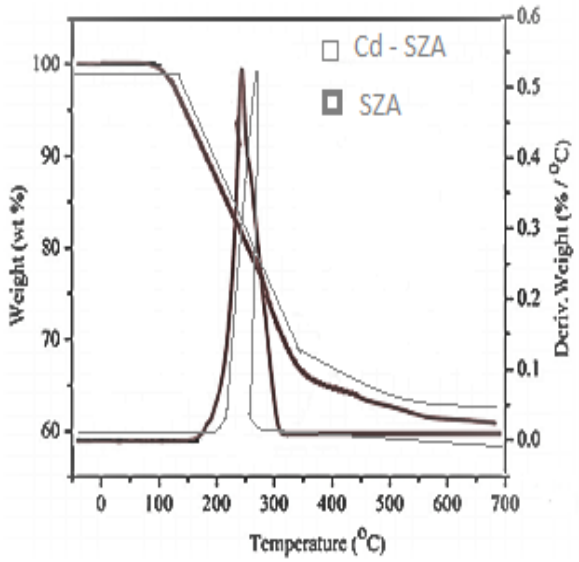

Fig. 6. TG-DTA analysis of SZA and Cd^{2+} doped SZA

3.6 SHG Efficiency Test

The grown crystals were powdered and NLO efficiency of the material was estimated by using Kurtz and Perry technique. The fundamental beam of Q-switched, Nd: YAG laser operating at 1.06nm and generating pulses of duration 35 ns and 10 Hz repetition. The well-known non-linear optical material standard KDP is taken as the reference material and the conversion efficiency of pure and Cd^{2+} doped SZA are 1.1 and 1.5 times that of KDP. The presence of Cd^{2+} 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 Cd^{2+} 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 both are crystallized 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 and have slight variation from both the materials. The TG/TDA analysis indicates that the presence of metal dopant (Cd^{2+}) slightly increases the decomposition temperature of SZA. The hardness test showed that the mechanical strength of Cd^{2+} doped SZA material was more than that of pure SZA. The Kurtz powder test proved that the Cd^{2+} metals have increased the efficiency of the SZA by approximately 0.5%. Based on these above observations both the pure and Cd^{2+} doped SZA materials can be used for the fabrication of photon devices.

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