Effect of Zn^{2+} on the structural, optical and magnetic properties of L-threonine cadmium acetate monohydrate single crystal

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Abstract

Single crystal of zinc doped L-threonine cadmium acetate monohydrate (LTCA); an organometallic optical crystal has been grown by slow evaporation technique. Structural parameters of the grown crystals are identified using the Single crystal X-ray diffraction. UV-Vis measurements were carried out to study the optical properties such as transmittance, reflectance, extinction coefficient and refractive index. The energy gap of the organometallic compound was estimated. The optical property confirms that the material is suitable for optical device fabrications. Functional groups present in the compounds are identified from Fourier transform infra red analysis. Magnetic behaviors of zinc doped crystals are confirmed by using vibrating sample magnetometer.

Keywords

Diamagnetic; Organometallic; Refractive index; Amino acid crystal.

1. Introduction

Organometallic compounds have at least one carbon to metal bond which can either σ bond of direct carbon to metal or π bond with a metal complex bond. The nature and character of metal carbon bond of organometallic compounds can behaved either as ionic, covalent or in between, which has very important roles in chemical reactions [1].Growth of organometallic amino acid crystal is an interesting field with the beginning of their applications in sensors, luminescence, ceramics, non linear optical, solid state laser and magnetic materials. In an organometallic metal organic frame the optical properties are dominated due to the organic ligands. Since metal compounds have high transparency in the UV region because of their closed d^{10} shell, there has been focus on the group (IIB) metals such as Zn and Cd [2]. Nonlinear optical crystals with high conversion efficiencies for second harmonic generation and transparent in the visible and ultraviolet regions are required for numerous device applications [3-7]. In this context, our group is interested to crystallize and analyze the organometallic compounds L-threonine cadmium acetate monohydrate. The molecular structure of the compound is already reported, which shows a polymeric supramolecular organization of the molecules [8]. Initial interest in the material is extended to analyze the properties such as thermal, optical, structural and magnetic properties. L-threonine cadmium acetate crystals have optical and excellent dielectric properties has been studied [9]. In this work, we are going to present the structural, optical and magnetic properties of the zinc doped LTCA crystal.

2. Materials and method

Zinc doped L-threonine cadmium acetate monohydrate, an organometallic compound crystallized by slow evaporation technique at the ambient temperature. The precursor materials used in the growth process are commercially available L-threonine, cadmium acetate dihydrade and zinc acetate. L-threonine and cadmium acetate solutes were taken in a stoichiometric ratio and completely dissolved in double distilled water. As above, 0.4 mole percentage of zinc acetate were added as a dopant and the solution was stirred well. The prepared solution was filtered, after 30 days good quality crystals harvested are shown in Fig.1.

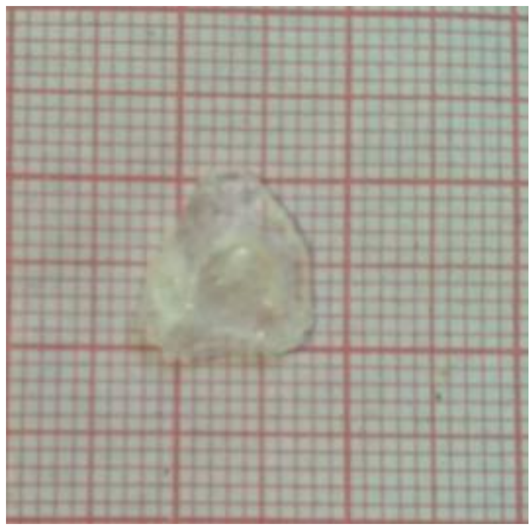

Fig. 1 Zn^{2+} doped LTCA crystal

The structure of the grown Zn^{2+} doped LTCA crystal was confirmed by using X-ray diffraction studies. The lattice parameters of the grown crystals were resolved from the single crystal X-ray diffraction analysis using a Bruker Kappa APES II single crystal X-ray diffractometer with MoKα (λ=0.71073 Å) radiation. UV-Vis spectrum has been recorded using UV spectrophotometer (ELICO) in the range of 200-1200 nm. Functional group present in the grown crystals are identified using Fourier transform infra red spectroscopy. The magnetic behavior of the zinc doped sample was depicted at room temperature by the applied magnetic field to a sample of mass 15.000 E^{-3} g in an average Time of 3 sec with the field increment of 500 G.

3. Result and Discussion

Zinc doped LTCA crystals are formed due to the chemical reaction between L-threonine, cadmium acetate and zinc acetate and the chemical scheme of the synthesized Zn^{2+} doped LTCA compound is shown in Fig. 2.

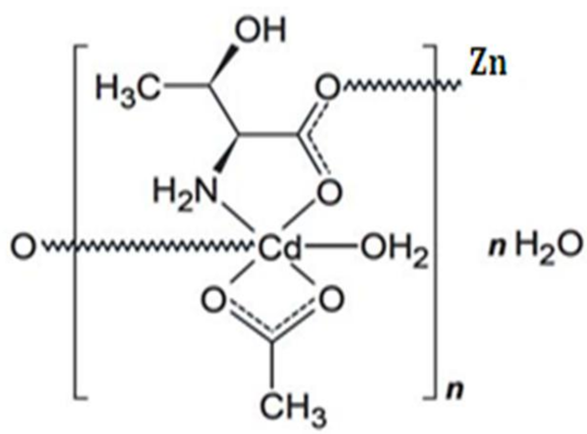

Fig. 2 Chemical scheme of Zn^{2+} doped LTCA

A single crystal X-ray diffraction study confirms that the grown Zn^{2+} doped LTCA crystal belongs to monoclinic crystal system. The lattice parameters are a = 5.87 Å, b = 8.87 Å, c = 10.81 Å, crystallographic axes $\alpha = 90^0$, $\beta=91.84^0$, $\gamma = 90^0$, volume = 563 $Å^3$ and space group $P2_1$. Optical transmission spectra of 2.36 mm thickness Zn^{2+} doped LTCA crystal recorded is depicted in Fig.3. From the graph it was known that the grown crystal have good transmittance percentage and the lower cutoff wavelength around 239.2 nm. The optical parameters are evaluated at the lower cutoff wavelength.

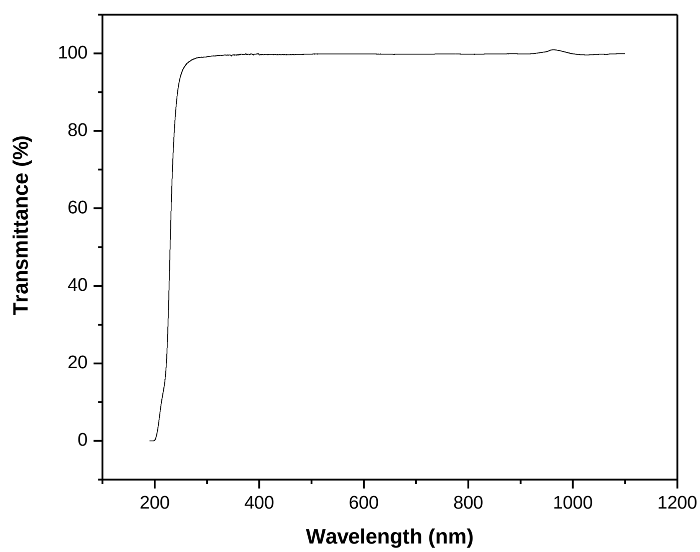

Fig. 3 UV spectra of Zn^{2+} doped LTCA crystal

The optical band gap (Eg) is evaluated at the lower cutoff wavelength (λ) for the crystal using the relation,

$$Eg = \frac{hc}{\lambda} \quad (1)$$

Valance and conduction band edge positions are evaluated by taking account of the electronegativity of the Zn^{2+} doped LTCA crystal (χ =7.0262). Furthermore, the position of the valance and conduction band of the Zn^{2+} doped LTCA crystal can be determined using the relations as follows;

$$E_{(CB)} = \chi - E^{c} - 0.5\,Eg \quad (2)$$

$$E_{(VB)} = E_{(CB)} + Eg \quad (3)$$

Where h is planks constant, c is the velocity of light. X represents absolute electronegativity of the Zn^{2+} doped LTCA compound. E^c denotes the energy of free electrons on the hydrogen scale (4.5 eV). Where $E_{(CB)}$, $E_{(VB)}$ are the band edge position of the valance and conduction band respectively. Refractive index is considered as a most significant optical property. The refractive index of the crystal is evaluated from the absorption coefficient (α), extinction coefficient (K) and reflectance (R) using the following relations;

$$\alpha = \frac{2.303 \times \log \frac{1}{T}}{t} \quad (4)$$

$$K = \frac{\lambda\alpha}{4\pi} \quad (5)$$

$$R = \frac{\exp(-\alpha t) + \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp}(-2\alpha t)T^2}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad (6)$$

$$\text{The refractive index, } n = -(R+1) + \frac{2\sqrt{R}}{R-1} \quad (7)$$

Table. 1 Calculated optical parameters of doped crystal

Band gap (eV)	$E_{(CB)}$ (eV)	$E_{(VB)}$ (eV)	Extinction coefficient 10^{-06}	Reflectance	Refractive index
5.184	-0.066	5.1182	3.65	1.42	3.21

The Fourier transform infra red spectrum of Zinc doped LTCA recorded was shown in Fig. 4. The broad vibrational band observed near 3355 cm^{-1} is assigned to the symmetric stretching mode (O-H) of the water molecule. The peak observed near 1577 cm^{-1} is attributed to CH_3 asymmetric stretching vibration of acetate and 1349 cm^{-1} is due to CH_3 asymmetric bending vibration of L-threonine. CH_3 asymmetric bending vibration observed around 1354cm^{-1}. CH_3 rocking is found near at 1190 cm^{-1}. The peak observed at 1032cm^{-1} is assigned to C-N stretching vibration. The peaks found at 943 cm^{-1} are due to stretching vibrations of C-C. Sharp peaks at 667cm^{-1} is due to OCO symmetric bending.

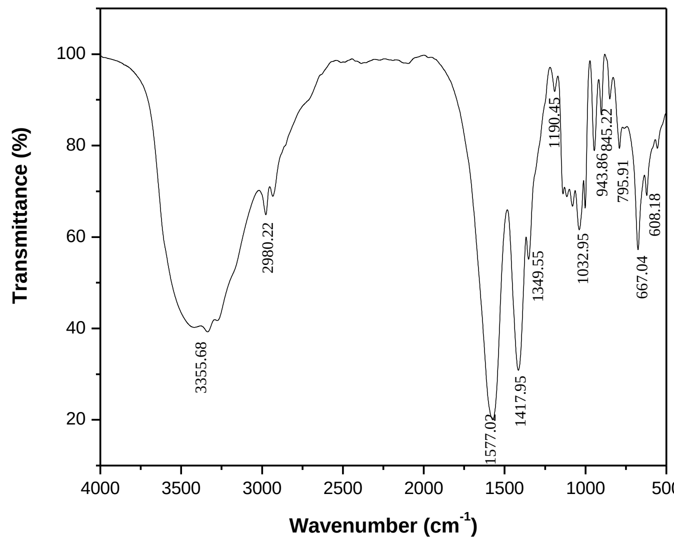

Fig. 5 FTIR spectra of Zn^{2+} doped LTCA

Magnetic behavior of the prepared zinc doped L-threonine cadmium acetate monohydrate compounds are identified by Vibrating Sample Magnetometer (VSM). Fig. 6 shows the field moment plot for zinc doped LTCA crystal. From the plot, it was known that Zn^{2+} doped LTCA shows diamagnetic nature with negative coercivity 404.26 G, retentivity12.836 E^{-6} emu and saturation magnetization 652.66 E^{-6} emu. Pure cadmium metal also behaves as diamagnetic nature due to completely filled electrons. Due to completely filled s-shell, zinc doped LTCA shows diamagnetic nature. Moreover, the magnetic properties remain same due to the addition of zinc (0.74 Å) with smaller ionic radius compared to cadmium (0.95 Å).

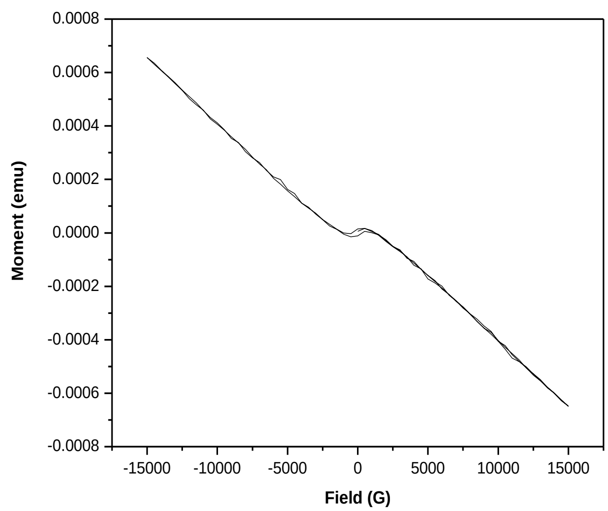

Fig. 5 M-H plot of Zn^{2+} doped LTCA

4. Conclusion

Organometallic compounds are widely used in homogeneous catalysis and find practical applications in both stoichiometric processes and medicinal biochemistry. An organometallic optical crystal, zinc doped L-threonine cadmium acetate monohydrate was successfully grown by slow evaporation technique. Single crystal X-ray diffraction studies confirm that the grown crystal belongs to monoclinic crystal system. The optical properties of the grown crystals have been analyzed from UV-Vis analysis and the optical band gap was found to be 5.184 eV. Diamagnetic nature was confirmed by Vibrating sample magnetometer. Thus the optical and magnetic study confirms that the grown crystal is semiconducting in natures used for magnetic storage applications.

5. References

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