Influence of Cu^{2+} Ions on the Structural, Optical and Magnetic Properties of Semiorganic L-Alanine Cadmium Chloride Single Crystal

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ABSTRACT: Most of the amino acids exhibit NLO properties. L-Alanine cadmium chloride (LACC) single crystal is one of the most popular crystals used for Nonlinear Optical (NLO) applications. In this paper, the effect of doping copper chloride in L-Alanine cadmium chloride crystal has been investigated. Copper chloride (Cu^{2+}) doped L-Alanine cadmium chloride crystals were grown by slow evaporation method at room temperature. Good quality and transparent Cu^{2+} doped LACC crystals were obtained. The grown crystal is characterized by using XRD analysis to confirm the structure of grown crystal. EDAX analysis confirms the presence of do pent Cu^{2+} in the host crystal LACC. Transmittance of the crystal was analysed using UV-Vis spectrum. Thermal stability and melting point of the doped crystal obtained from the TG/DTA analysis. The micro hardness values are found from the Vicker's hardness test. The magnetic properties of the crystal were also reported using vibrating sample magnetometer analysis.

Keyword: Solution growth, XRD, EDAX, VSM.

1. INTRODUCTION

The inability of organic materials to grow to large crystal sizes impedes device fabrication, which has led to the discovery of a new class of crystals called semi organics to satisfy technological requirements [1,2]. The most promising candidates among metal-organic compounds have attracted researchers in recent years due to their various properties such as NLO response, magnetism, and luminescence, as well as applications in photography and drug delivery [3] due to the combination of organic and inorganic components. In semiorganic materials, the organic ligand is ionically bonded with the inorganic host, which promotes exceptional mechanical strength and chemical stability [4]. Moreover, metal– organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the coordinated metal centre [3]. L-Alanine cadmium chloride is a promising NLO compound. Optical properties of L-alanine cadmium chloride single crystal studied by Suresh sagadevan and R.Varatharajan [5]. The electrical parameters and the corresponding activation energies have been reported by Bright and Freeda [6]. Study of the influence of doping on several crystals can modify the physical properties of materials for technological applications and the effect of various dopants on L-alanine cadmium chloride has been reported [6-8].

2. CRYSTAL GROWTH

The title compound was synthesized by dissolving (AR grade) L-alanine and cadmium chloride in a 1:1 molar ratio. After continuous stirring for about 2 hours using a magnetic stirrer, 0.7 mole % of copper chloride is added to the above solution. The mixture was subjected for heating below an optimum temperature of 60° C in a temperature controlled water bath to dry the sample. It was completely dissolved in double distilled water to form a saturated solution. Tthe supersaturated solution was filtered with Whatmann filter paper and kept it in a dust free atmosphere. The saturated solution was allowed to dry at room temperature by the slow evaporation technique. After a period of 30 days, optically transparent and defect free crystals with dimensions of 15 × 10 × 3 mm^3 were grown, and the photograph of the grown crystal is shown in Fig. 3.1.

Fig 1. As grown Cu^{2+} doped LACC crystal

3. RESULTS AND DISCUSSION

3.1. Powder X-ray diffraction

Powder X-ray diffraction spectra were recorded in PANanalytical Xpert - pro instrumentation. Continuous scanning was applied with a slow scanning speed (step size = 0.05 °) and small time constant (step time = 10.138 s). The XRD pattern of copper chloride doped L-alanine cadmium chloride is shown in Fig.2. Sharp and high intensity diffraction peaks indicate good crystalline nature of the grown crystal.

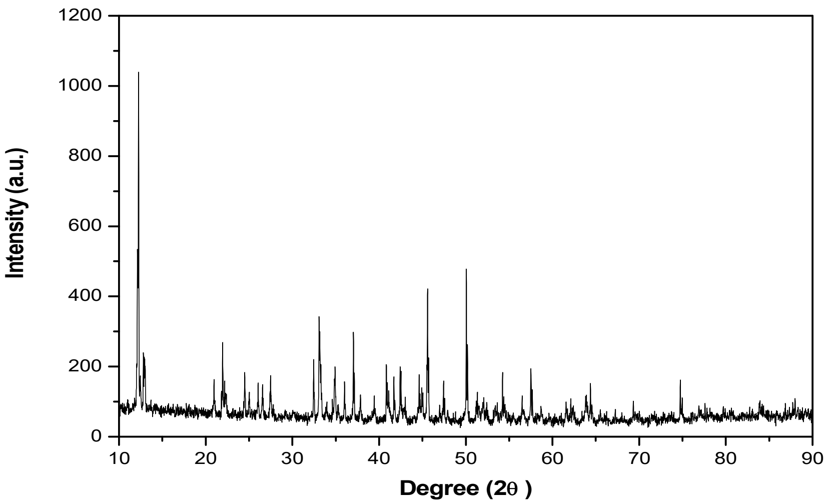

Fig 2. XRD Pattern of Copper doped LACC crystal

3.2. Single crystal XRD

Single Crystal X-ray Diffraction (SXRD) analysis for pure LACC was observed using ENRAF–NONIUS CAD4-MV31 Bruker Kappa APEX11 diffractometer. The single crystal XRD of pure LACC crystal reveals that the crystal belongs to monoclinic system with non centrosymmetric space group C_2.The lattice parameters of the grown crystal obtained using the 'unit cell software' and is given in Table 1. SXRD data reveals that the dopent Cu^{2+} ion does not alter the crystal structure, but it enters into the crystal lattice of pure LACC.

Table 1. Lattice parameters of Cu^{2+} doped LACC

Unit vector (Å)	Angles (°)	Volume (Å³)
a=16.28 Å b=7.32 Å c=7.96 Å	α=90.00° β=116.80° γ=90.00°	848

3.3. EDAX Analysis

EDAX analysis has been recorded using Bruker Nano German. Energy peaks correspond to the various elements present in Cu^{2+}doped LACC crystal is shown in the Fig.3.

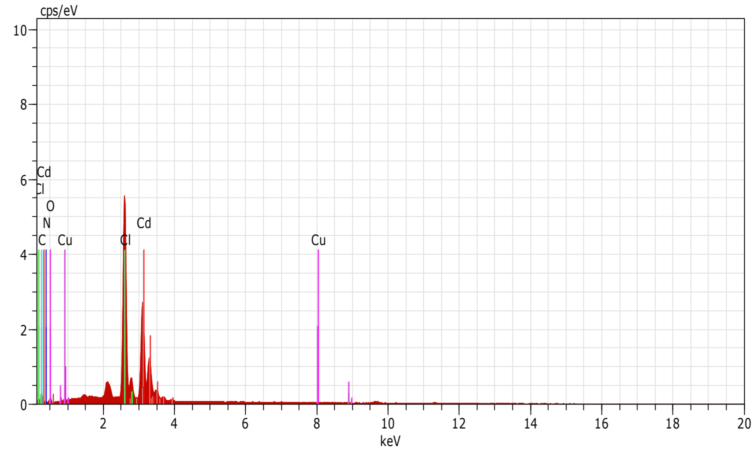

Fig 3. The EDAX spectrum of Copper doped LACC crystal

The composition of all the elements and the percentage of atoms present in the compound are given in Table 2. Hence, it is clear that the Cu^{2+} ions are successfully doped into the crystal lattice of LACC. The ingestion of dopants in the host lattice was well confirmed by EDAX Analysis.

Table 2. Elemental composition of Cu^{2+} doped LACC

El	AN	Series	unn[wt.%]	C norm [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
Cd	48	L-series	40.50	50.27	16.50	1.28
Cl	17	K-series	25.46	31.61	32.88	0.89
C	6	K-series	8.97	11.13	34.18	1.85
N	7	K-series	1.54	1.91	5.04	0.55
O	8	K-series	3.95	4.90	11.30	0.97
Cu	29	K-series	0.14	0.17	0.10	0.04

3.4. UV-visible study

The UV–Vis spectrum analysis has been measured using a Systronics Double Beam UV–Vis spectrophotometer 2201. The recorded UV-visible transmittance spectra of 0.7 mol % Cu^{2+} doped LACC crystal is shown in Fig.4.

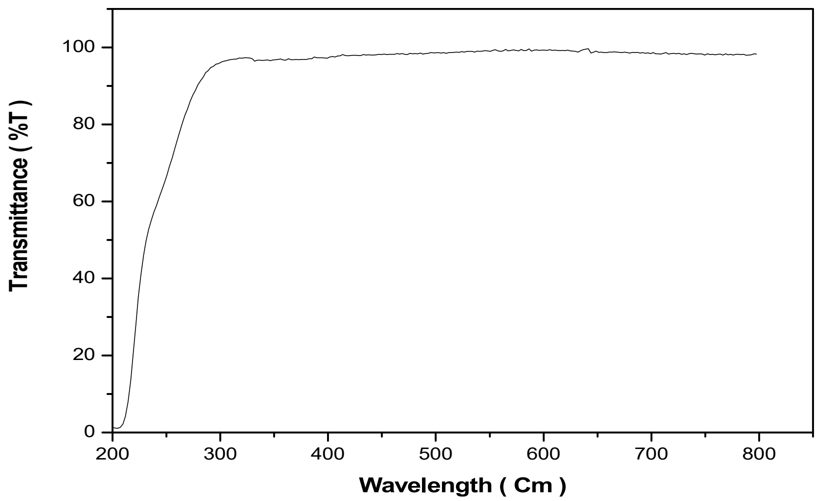

Fig 4. Optical transmittance of Cu^{2+} doped LACC crystal

As observed in the spectrum, the percentage of transmission in the visible region is high for Cu^{2+} doped LACC crystal which is a required property for NLO material. The lower cut-off wavelength for doped crystals is 228 nm. The lower cut-off wavelength for the grown crystals in the transmittance spectra lies between 200nm and 400 nm which is a desired requirement for crystals capable of generating blue light by SHG from diode lasers [9]. Hence it is a good candidate for NLO applications. The energy gap (E_g) is an important feature of materials which determines their applications in optoelectronics. The absorption spectra method is direct, main and simple method for probing the energy band structure of semi-conductor. The absorption spectra of Cu^{2+} doped LACC crystal and its corresponding Tauc plot (inner plot) is shown in Fig 5. The band gap energy of the samples are measured by the extrapolation of the linear portion of the graph between the modified Kubelka-Munk function$(\alpha h\nu)^2$ versus photon energy ($h\nu$) [10].

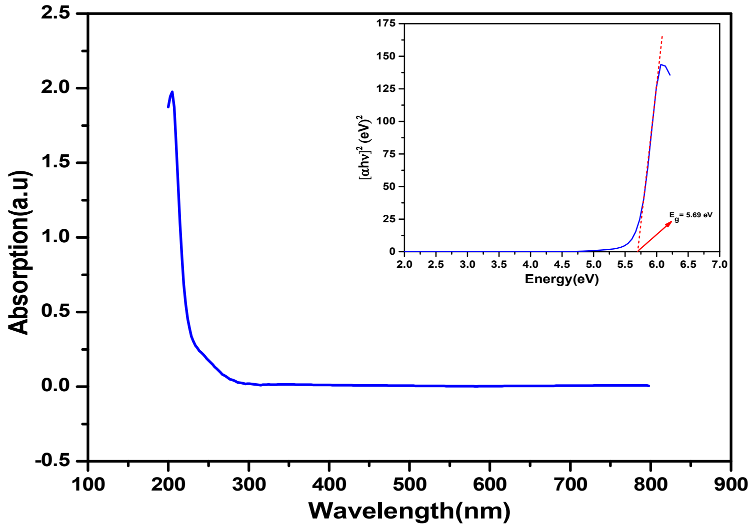

Fig. 5. UV-Vis absorption spectrum of 0.7 mol% Cu^{2+} doped LACC

The energy gap as calculated for Copper chloride doped LACC crystal is 5.7 eV. The increase of the energy gap for semiconductors lead to decreases the absorption region and the substance may be transparency and the absorption edge shifted towards low wavelengths. This may be useful for solar cell applications [11].

3.5. Thermal studies

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) for copper doped LACC has been recorded using a simultaneous Perkin Elmer STA 6000 thermal analyzer. A ceramic crucible was used for heating the sample and the analyses were carried out in an atmosphere of nitrogen in the temperature range 100–750 °C. The TGA/DTA curve of the sample crystal is illustrated in Fig. 6.

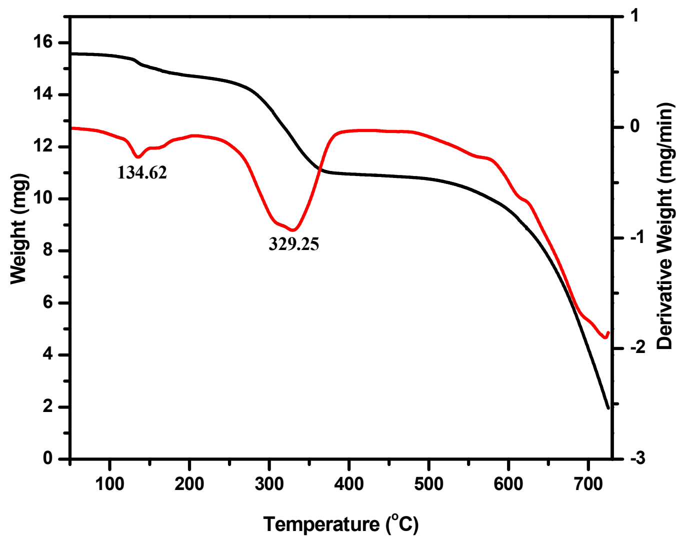

Fig. 6. TG/DTA Thermogram of 0.7 mol% Cu^{2+} doped LACC

From the DTA curves it is inferred that the decomposition of of 0.7 mol% doped Cu^{2+} takes place in the vicinity of 117.09 °C. The sharpness of this endothermic peak shows the good degree of crystallinity and purity of the sample. The other endothermic peak at 329.25°C reveals the decomposition of LACC structure and coincide with the decomposition observed in TGA curve. From the TGA curve, it can be seen that there was gradual weight loss between 240.66 °C – 375.0 °C (21.4%) and 248.25 °C – 375.19 °C (22.3%). It is seen that at different stages, various gases like CO, CO_2, NH_3, Cl_2 etc., are liberated leading to bulk decomposition of the compound. In the TGA thermogram, slight changes in the melting point between pure and doped LACC crystals account for the incorporation of dopants into the LACC lattice. The thermal stability and melting point for Cu^{2+}doped crystals are 134.62 **^{0}C** and 117.1 **^{0}C.** As is observed the thermal stability of doped crystal is higher than that of pure LACC crystal.

3.6. Magnetic studies

To understand the magnetic properties of the grown crystal, it is characterized using vibrating sample magnetometer (VSM). VSM analysis was carried out using Lakeshore: model: 7404. The magnetic behavior of the as grown crystal is traced at room temperature (27° C) using a magnetic field (H) in the range of -12 K Oe to 12 K Oe is depicted in Fig.7.

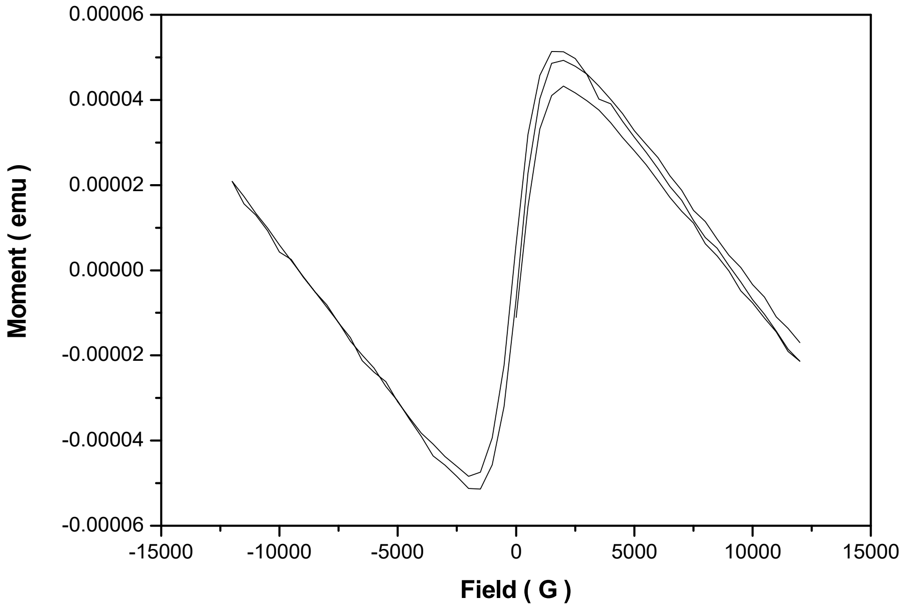

Fig 7 . The magnetic field vs moment curves of Cu^{2+} doped LACC crystal

The hysteresis loop displays the characteristic of soft ferromagnetic magnetic materials. Cu^{2+} is the most stable state. It has the electronic configuration d^9 and has an unpaired electron. If the two copper ions form a metal-metal bond these electrons will be paired and the complex will be diamagnetic. If they do not form a bond then the complex will be paramagnetic. Its compounds are paramagnetic [12]. There is no hysteresis loop formed. But the diamagnetic nature is reduced, also not ferromagnetic. So from the VSM due to the addition of a few Cu^{2+} ions to pure LACC, little magnetism exists, that may be paramagnetic.

The values of the magnetization, coercivity and retentivity are 51.36 E^{-6} emu, 4619.0G and 6.4676 E^{-6} emu respectively. The reason for the decrease in magnetization may also be due to the fact that low Cu^{2+} concentration reduces the number of spins occupying the sublattices, causing the net magnetization to increase. Smaller magnetization, in the case of 0.7 mol% Cu^{2+}doped LACC is expected due to the surface disorder and modified cationic distribution [13].

4. CONCLUSION

Single crystals of pure and Copper Chloride doped L-Alanine Cadmium Chloride were grown successfully by slow evaporation technique. Powder XRD analysis shows good crystalline nature of the grown crystal. Single crystal X-ray diffraction studies were carried out, and the lattice parameters are tabulated. EDAX studies confirmed the presence of the dopant in the host crystal. UV-VIS-NIR studies reveal that the doped crystals possess wide transparency in the entire visible region. The Cu^{2+} doped LACC has band gap energy of 5.7 eV. The thermal analysis shows that the Cu^{2+} doped LACC crystal has higher thermal stability than pure LACC. The magnetic studies reveal that the Cu^{2+} doped LACC is paramagnetic in nature.

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