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Synthesis, Growth and Characterization of Magnesium Chloride Doped L-Alanine Cadmium Chloride Single Crystal: For Nonlinear Optical Application

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ABSTRACT

The aim of this research was to synthesize and characterize pure and magnesium chloride ($MgCl_2$) doped L–alanine cadmium chloride (LACC) single crystals. Pure and $MgCl_2$ doped LACC single crystals were synthesized by solution method with slow evaporation solution growth technique at room temperature. The single crystal X-ray diffraction studies of pure, 1 and 2 mol% $MgCl_2$ doped LACC single crystals revealed monoclinic crystal structure with C_2 space group. The optical properties of pure and $MgCl_2$ doped LACC single crystals investigated by UV–VIS/NIR spectrometer confirmed that the crystals were transparent in the wavelength range of 230-1100 nm. The optical band gap energy of pure and doped LACC single crystals were found to have the same value of 5.4 eV. The energy dispersive X-ray analysis indicated the incorporation of magnesium and chlorine atoms in LACC single crystal. The second harmonic generation efficiency of 1 and 2 mol% $MgCl_2$ doped LACC crystals were analyzed by Kurtz-Perry powder technique and found to be 1.75 and 2 times greater than that of the standard potassium dihydrogen phosphate crystal, respectively.

INTRODUCTION

The core attention of nonlinear optical (NLO) studies is to modify the phase, frequency or amplitude of intense electromagnetic input field using NLO materials for photonic applications (Boyd, 2019). Nonlinear optical materials have been the subject of much research in recent years due to their potential uses on optical computing, laser technology, harmonic generation, optical communication, optical data storage technology, signal processing and manipulation. Therefore, currently there is a need to produce high efficiency single crystals of NLO materials (Marudhu *et al*., 2013; Raguram *et al*., 2016). Much attention has been paid to organic NLO materials due to their promising properties, such as fast optical response time and high nonlinearity, compared to the inorganic materials. The aggregate of materials which have large nonlinear optical properties with resistance to physical and

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chemical attack has led to the investigation of semi-organic materials (Kaliammal *et al*., 2020). Amino acids are favorable organic materials displaying specific features of interest, such as molecular chirality which secures non-centrosymmetric crystallographic structure, absence of strongly conjugated bonds which leads to wide transparency ranges in the visible and ultra-violet spectral regions and zwitter ionic nature of the molecule which favors crystal hardness for applications in devices (Natarajan *et al.*, 2006; Raguram *et al*., 2016). L-alanine is an amino acid group that forms a chains of complexes upon reaction with different acids.

Reports are available on L-alanine based NLO crystals such as: L-alanine cadmium chloride (Dhanuskodi *et al*., 2007), L-alanine acetate (Kumar *et al*., 2005), L-alanine Hydrogen chloride (Rose *et al*., 2010), L-alanine sodium nitrate(Fleck and Petrosyan, 2009), L-alanine potassium chloride (Prabha and Palaniswamy, 2010) and L-alanine maleate (Karunanithi *et al*., 2012). L-alanine cadmium chloride is an amino acid derivative NLO material with high second harmonic generation (SHG) efficiency and it crystallizes in the monoclinic crystal system with non-centrosymmetric space group (Jothimani and Selvarajan, 2017; Radhika *et al*., 2013).

Few reports are available on the synthesis of L-alanine cadmium chloride single crystals by solution growth method. As far as the authors are aware, there is no report on magnesium chloride doped L-Alanine cadmium chloride single crystals. Since doping can influence many of the useful properties like, optical transparency, second harmonic generation (SHG), crystalline perfection which may in turn influence the physical properties depending on the degree of doping and the accommodating capability of the parent crystal (Shkir *et al*, 2014). Magnesium chloride-doped L-alanine cadmium chloride single crystals were grown using slow evaporation, and their structural, optical, second-harmonic generation (SHG), and compositional properties were characterized.

MATERIALS AND METHODS

In this work, analytical grade L-Alanine (Sisco Research laboratories, 99%), cadmium chloride (Uni-CHEM, 99%) and magnesium chloride (Uni-CHEM, 98%) were used directly without further process. The parent compound was synthesized by taking an equimolar ratio of L-alanine and cadmium chloride that is obtained by dissolving 8.0901 g L-Alanine and 22.8353 g cadmium chloride. The calculated amount of L-alanine has been dissolved with distilled water in a beaker and placed on a magnetic hot plate regulated at 30°C then cadmium chloride was added. It has been stirred continuously for four hours to obtain homogenous supersaturated solution. Afterwards the solution has filtered by using Whatman filter paper into a 500 m1 beaker. The filtered solution has been kept free from dust and other contamination by covering it with porous cover so the rate of evaporation could be minimized. 1 mol% and 2 mol% $MgCl_2$ doped L-Alanine cadmium chloride single crystals were synthesized by adding 2.0333 g and 4.0666 g $MgCl_2$ into the parent compound solution respectively. A similar stirring process has been followed for 1 and 2 mol% of $MgCl_2$ doped L-alanine cadmium chloride. After a period of 30 days, optically clear transparent crystals were harvested from supersaturated solution. Accordingly, the grown pure, 1 and 2 mol% $MgCl_2$ doped LACC crystals were shown in Fig. 1.

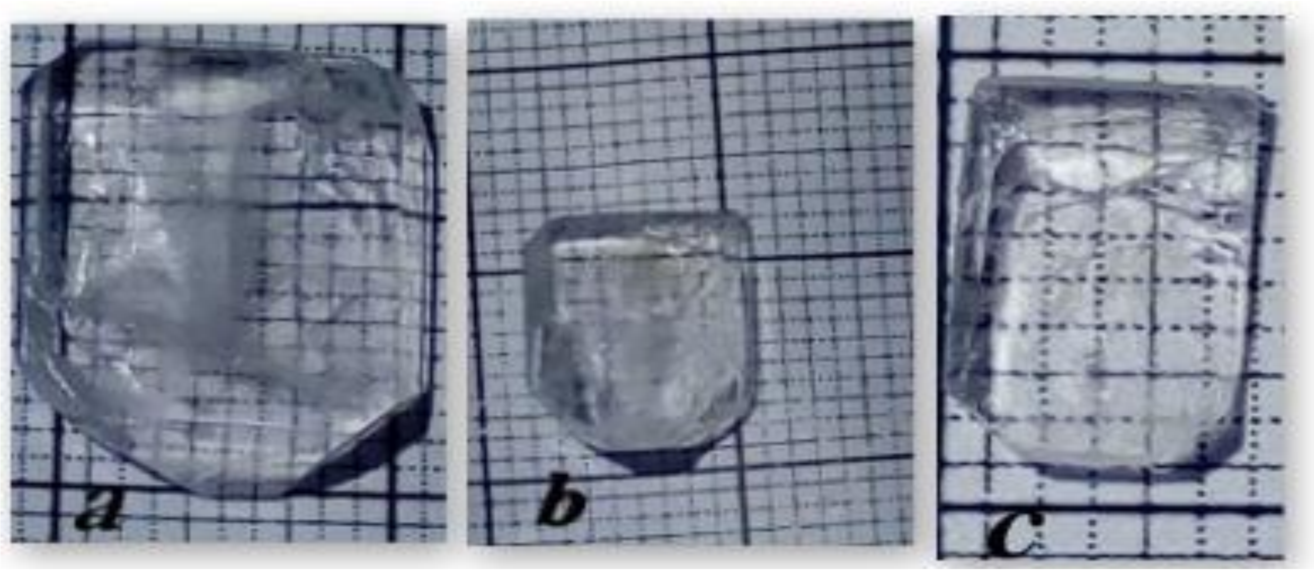

Fig. 1. Photograhp of (a) undoped, (b) 1 mol% $MgCl_2$ doped and (c) 2 mol% $MgCl_2$ doped LACC single crystals respectively.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction

Single-crystal X-ray diffraction (XRD) analysis using a Bruker AXS Kappa APEXII diffractometer (Mo Kα radiation, λ = 0.07107 nm) revealed that 1 and 2 mol% $MgCl_2$-doped LACC crystals adopted a monoclinic structure (with interaxial angles in a crystal lattice of α≈ β ≈ 90° and γ ≈ 116.41°). The calculated lattice parameters (Å) were a = 16.282, b = 7.261, c = 8.008 for 1 mol% and a = 16.286, b = 7.268, c = 8.011 for 2 mol% $MgCl_2$ doping. The unit cell parameters and crystal structure for pure LACC crystal in (Å) were a = 16.298, b = 7.259, c = 7.981 and monoclinic respectively as reported by other authors (Dhanuskodi *et al.*, 2007). It is observed that both undoped and $MgCl_2$ doped LACC crystals crystallize in same structure however, slight change in the lattice parameters were detected from the doped crystal compared to the pure LACC crystal. The changes in the lattice parameter may be due to the incorporation of $MgCl_2$ in LACC crystal lattice. The grown crystals belongs to space group C_2 which is recognized as non-centrosymmetric**,** thus satisfying an essential material criteria for the SHG activity of the crystal (Fentaw *et al.*, 2019).

UV–Vis NIR analysis

To assess its optical properties, the transmission, cutoff wavelength, and band gap energy of the NLO single crystal were determined. In this study these optical parameters have been studied by using Perkin Elmer Lambda 35 UV-VIS-NIR spectrophotometer in the wave length range between l90-ll0 nm to cover near ultraviolet, visible and near IR regions. The recorded spectrums were shown in Fig.2.

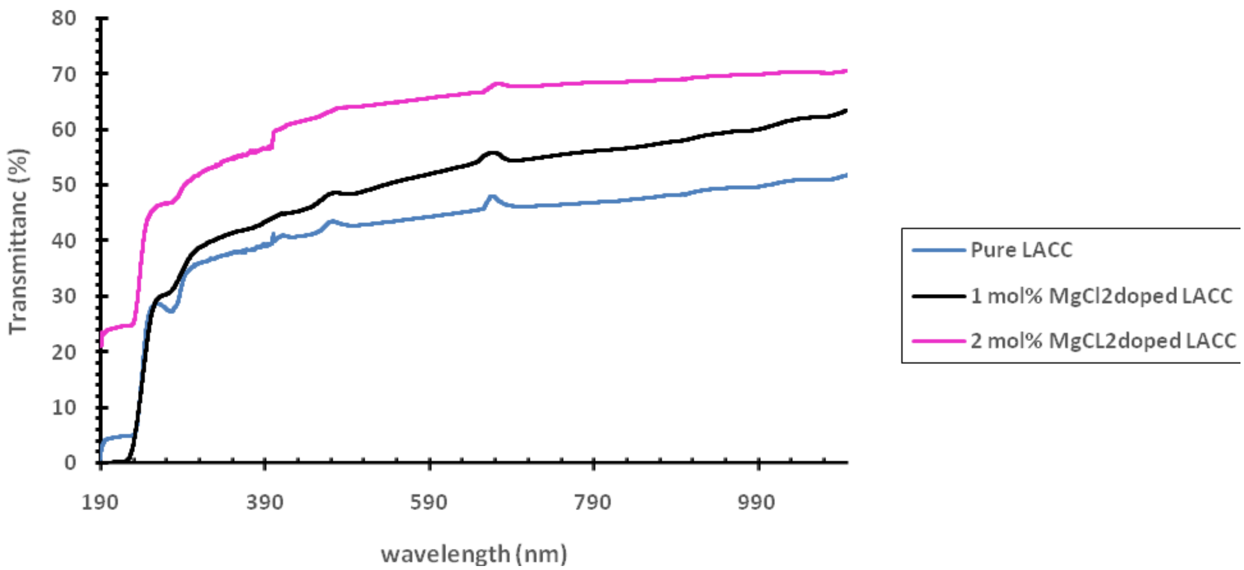

Fig.2. Optical transmittance of pure, l and 2 mol % of $MgCl_2$ doped LACC crystals.

From the spectrum it is detected that the crystals were transparent in the wavelength range 230 - 1100 nm. NLO materials can be of practical use only if they have a wide transparency range, thus the optical transmittance range of the grown crystals make them convenient materials for nonlinear optical applications (Ahlam *et al., 2013;* Charoen-In *et al.*, 2010). The result confirmed that the lower cutoff wavelength of the crystals were almost the same irrespective of the dopant concentration, however, the percentage of transmittances have increased for 1mol% and 2 mol% $MgCl_2$ doped LACC crystal. The increase in optical transmittance could be due the enhancement in the crystalline quality and absence of major defects as crystalline defect affect the optical properties (Jothimani and Selvarajan, 2017). The band gap energy was calculated using the relation $E_g = 1240/\lambda_{min}$, where λ_{min} is the cut-off wavelength of the light which is 230 nm and it was found to be 5.4 eV for pure and doped crystals (Raguram *et al.*, 2016).

Energy dispersive X-ray spectroscopy (EDX) analysis

Energy dispersive X-ray spectroscopy (EDX) is a very useful instrument that used to identify the elemental composition of the samples. The incorporation of 1 and 2 mol% of $MgCl_2$ into the crystal lattice of LACC was confirmed by JEOL-6390LV scanning electron microscope attached to EDX and it is shown in Fig.3. The EDX spectrum confirmed existance of expected elements such as oxygen, chlorine, magnesium and cadmium in both 1 and 2 mol% of $MgCl_2$ doped LACC crystal. The molecular weight and atomic percentage of identified elements in the doped NLO samples were presented in Table1. The measurable (quantitative) and qualitative EDX results clearly showed increase in the atomic percentage of Mg and Cl signifying incorporation of the $MgCl_2$ in the LACC single crystal structure.

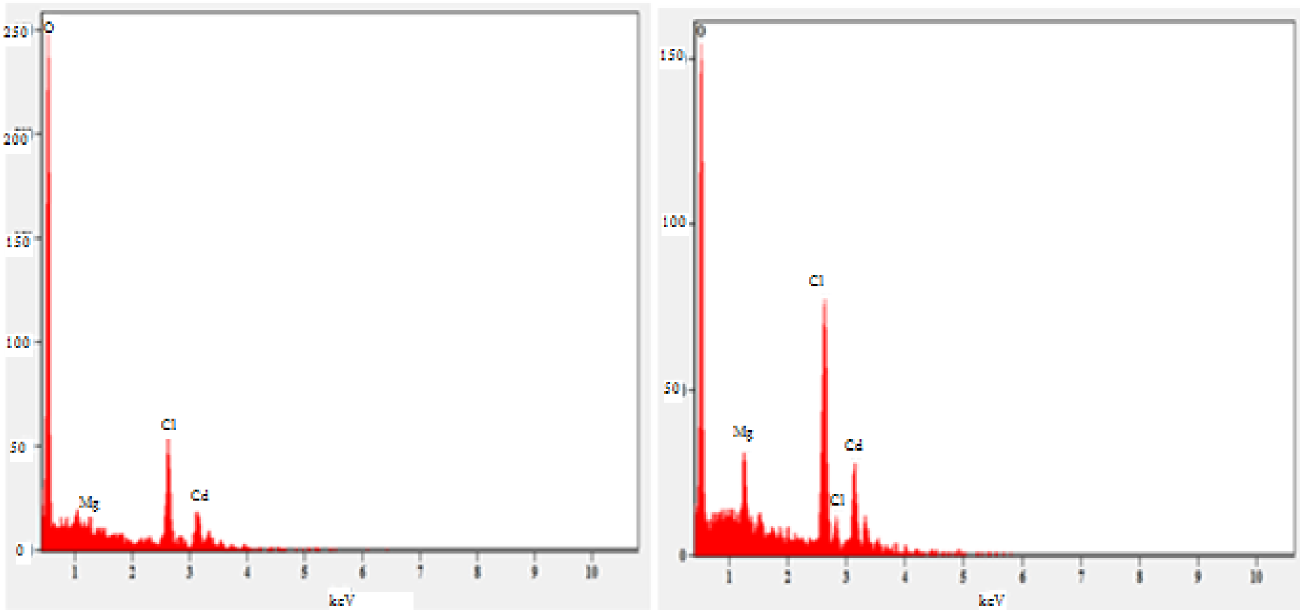

Fig. 3. EDX spectrum of 1 and 2 mol% of $MgCl_2$ doped LACC crystals respectively.

Table 1: Energy dispersive X-ray (EDX) analysis

Elements	1mol%$MgCl_2$+LACC		2mol%$MgCl_2$ +LACC	
	Weight%	**Atom%**	**Weight%**	**Atom%**
OK	74.28	91.19	62.49	82.57
MgK	0.72	0.57	5.41	4.70
ClK	10.20	5.65	16.38	9.77
CdL	14.80	2.59	15.72	2.96
Total	100.00	100.00	100.00	100.00

Second Harmonic Generation (SHG) test

The second harmonic generation efficiency analysis of the samples were carried out by Kurtz-Perry powder technique by packing very fine powder of $MgCl_2$ doped LACC sample in a microcapillary tube and a fundamental beam (1064 nm) from Nd-YAG laser was incident on the $MgCl_2$ doped LACC crystals (Kushwaha *et al*., 2011). A second harmonic generated green light beam (532 nm) was emerged from the samples. To evaluate second-harmonic generation (SHG) properties, potassium dihydrogen phosphate (KH_2PO_4, KDP) powder was used as a standard reference material. The transmitted beam voltage through KDP was then measured to be 12 mV. In comparison, the transmitted beam voltages through the 1 and 2 mol% $MgCl_2$-doped LACC samples were 21 mV and 24 mV, respectively. The SHG efficiency of the 1 and 2 mol% $MgCl_2$-doped LACC crystals was thus calculated to be 1.75 and 2 times greater than that of the KDP reference material. The SHG efficiencies of pure LACC single crystal was 0.87 times greater than that of the standard KDP crystal reported by (Kalaiselvi *et al*., 2013). The enhancement of SHG efficiency may be either due to the improved in crystallinity or the change in electronic structure of LACC crystals due to the doping of $MgCl_2$ (Bhagavannarayana and Kushwaha, 2010). The current results indicate that 1mol% and 2mol% $MgCl_2$ doped LACC crystals are the better candidates for NLO applications than the undoped LACC single crystal.

CONCLUSION

Pure and $MgCl_2$-doped (1 and 2 mol%) LACC single crystals were grown by slow evaporation at room temperature. Characterization included single-crystal XRD (confirming a monoclinic structure, space group C2), UV-Vis-NIR spectroscopy (showing high transmission across the UV-Vis-NIR range, enhanced by $MgCl_2$ doping), energy-dispersive X-ray spectroscopy (EDAX, confirming $MgCl_2$ incorporation), and second-harmonic generation (SHG) efficiency measurements (1.75× and 2× greater than KDP for 1 and 2 mol% doping, respectively). These results suggest that both pure and $MgCl_2$-doped LACC crystals are promising candidates for nonlinear optical applications.

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