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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF $CaCl_2$ DOPED ORGANOMETALLIC L-ASPARAGINE CADMIUM CHLORIDE MONOHYDRATE (LACCM) CRYSTALS

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ABSTRACT

Single crystals of Calcium chloride ($CaCl_2$) doped organometallic nonlinear optical material L-asparagine cadmium chloride monohydrate (LACCM) were successfully grown by slow evaporation method at room temperature. Grown crystals were characterized by single crystal and powder X-ray diffraction analysis, scanning electron microscopy and energy-dispersive analysis by X-ray. The second harmonic generation was confirmed by the Kurtz and Perry powder technique. The presences of various functional groups were identified from FTIR spectral analysis. DSC analysis revels it is thermally stable upto 400°C

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INTRODUCTION

Organic nonlinear optical crystals have recently attracted high attention because of their superior properties such as larger susceptibility, faster response and capability to design on the molecular level; however, unlike inorganic NLO crystals they have not come into a wide use due to some drawbacks such as difficulty to grow larger perfect crystals, and troubles in cutting and polishing of the device. Under this circumstances, the complex type crystals of organic-inorganics with NLO effects are developed which are expected to not only retain high nonlinear optical effects but also cut down some shortages of pure organic crystals, in other words, which have both advantages of organic and inorganic crystals with their physicochemical properties. However, the implementation of single crystals of organic materials in practical device-applications has been impeded by their inadequate transparency, poor optical quality and low LASER threshold. Inorganic crystals have excellent mechanical and thermal properties, but they possess relatively modest nonlinearity because of the lack of p electron delocalization. Hence, recent search is concentrated on organometallic materials due to their large nonlinearity, high resistance to LASER induced damage, low angular sensitivity and good mechanical hardness (Xing *et al.* 1987, Velso *et al.* 1990, Joseph John *et al.* 2007). Nowadays the organic and inorganic materials are being replaced by semiorganic materials because they share the properties of both organic and inorganic materials. Also the semiorganic materials show large nonlinearity, low angular sensitivity and good mechanical hardness. In the case of metalorganic coordination complexes the organic ligand is usually more dominant in the nonlinear optical (NLO) and dielectric effects. The metallic part focus is on group II B metals (Zn, Cd and Hg). These compounds usually have high transparency in UV region, because of their closed d10 shell. Potential NLO materials like bis thiourea cadmium chloride (BTCC), triallyl-thiourea cadmium chloride (TATCC) (Jiang *et al.* 1999) are examples of this approach. Among the few reports already published concerning the field of amino acid crystal simulations, some of them have presented results suggesting that alanine, leucine, isoleucine, proline and glycine(Tulip *et al.* 2005, Caetano *et al.* 2005, Flores *et al.* 2008, Jayaprakash Manoharan 2011a, 2011b) are wide band gap semiconductors, while valine and cysteine could be small band gap isolators; (Tulip *et al.* 2005, Candido Junior *et al.* 2011) on the other hand, it was suggested that anhydrous L-aspartic crystals behave as wide-gap semiconductors with higher carrier mobilities for directions parallel to the L-aspartic acid molecular layers, (Silva *et al.* 2012) while anhydrous L-serine crystals behave like n-type wide gap semiconductors

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(Costa *et al*. 2013). Besides, it was also pointed out that anhydrous crystals of DNA bases are wide gap semiconductors (Maia *et al*. 2011). The characterization of the band gap of these molecular materials and their charge transport properties, which depends on their band structures, are relevant for the development of bioorganic electronic and optoelectronic devices, (Irimia Vladu *et al*. 2011) as well as bionanoelectronics, (Parpura 2012) which could advance the development of sustainable, biodegradable, biocompatible, low-cost, and mass production electronic components. However, a few complexes incorporating incorporating L-aspargine cadmium chloride have been synthesized and studied (Masilamani *et al*. 2012, Srinivasan 2013). In our present work aiming to improve second harmonic efficiency, calcium chloride doped the single crystals of LACCM were grown by slow evaporation technique characterized and reported.

Experimental Procedure

Synthesis and growth of $CaCl_2$ doped LACCM

The title compound was synthesized from of L-aspargine and cadmium chloride monohydrate taken in equimolar ratio. The calculated amount of the reactants were thoroughly dissolved in double distilled water. Then, it was mixed with continuous stirring for about 2 h using magnetic stirrer with hot plate. One mole percentage of calcium chloride was added to the supersaturated aqueous solution prepared in a 100 ml beaker (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition by slow evaporation technique (Joseph John *et al*. 2008, Sivakala *et al*. 2014, 2016, Joseph John 2016a, 2016b, Selvarajan *et al*. 2011). The temperature and volume were kept constant, respectively at 30°C and 20ml for all the crystal growth experiments. After the completion of growth, crystals were harvested. Good quality optically transparent large size crystals were selected for carrying out the measurements.

Characterization

The single crystal X-ray diffraction studies of the grown crystals were carried out using BRUKER KAPPA APEX II model single crystal X-ray diffractometer with MoKα (λ = 0.717 Å) radiation. Powder X-ray spectrum was obtained by PANalytical X'Pert Pro Powder X'Celerator Diffractometer. FTIR studies of the grown crystals were analyzed by Fourier Transform Infra Red spectrometer model SPECTRUM RXI make PERKIN. The optical transmittance spectrum was recorded in the range of 190-1100 nm, using Lamda35 Perkin Elmer make UV-Vis-NIR spectrometer. The NLO test of LACCM crystals were evaluated by the Kurtz and Perry powder technique (Kurtz *et al*. 1969) using a Q-switched, mode locked Nd : YAG laser emitting 1.06µm, 8 ns laser pulses with spot radius of 1 mm. DSC measurements were done by Mettler Toledo DSC 822E model calorimetry.

RESULT AND DISCUSSION

Crystals with regular shape and size of about 14×11× 5 mm^3 were harvested within 15 to 20 days. The photograph of the grown LACCM crystals is displayed in Fig. 1. Morphology of crystals changes when growth conditions such as growth media, temperature and addition of impurities are altered. Since the growth temperature has not been completely kept constant during the growth of the crystals in the present work, there are morphological changes in the grown crystals.

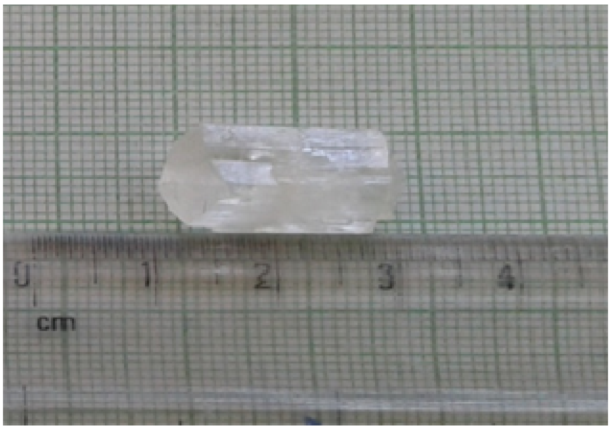

Fig. 1. The photograph of grown 1 mol% $CaCl_2$ doped LACCM crystal

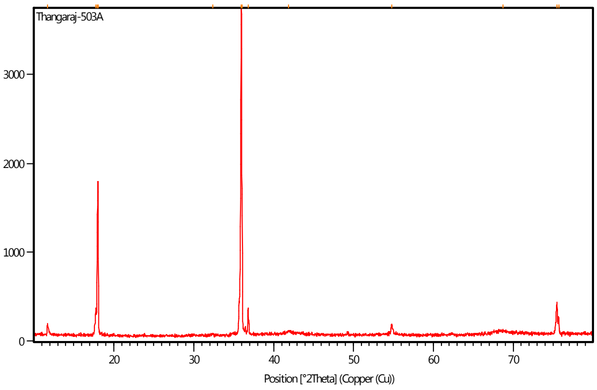

Fig. 2. XRD pattern of 1 mol% $CaCl_2$ doped LACCM crystal

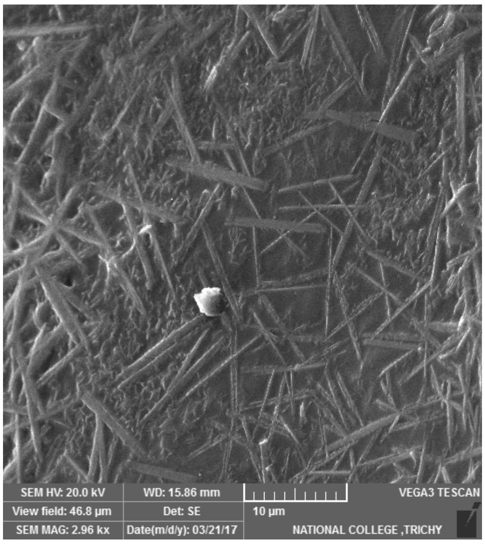

Fig. 3. SEM image of 1 mol% $CaCl_2$ doped LACCM crystal

Structural analysis

Crushed powder of LACCM crystal was subjected to powder X-ray diffraction analysis. The sample was scanned the wide range of 0–80 with a scan rate of 2 /min. The recorded X-ray pattern of LACCM is shown Fig 2. The prominent well defined sharp Bragg's peak at specific 2θ angle reveals that the good crystalline nature of $CaCl_2$ doped LACC crystal. Crystal size of 0.200 x 0.200 x 0.300 mm and wave length 0.71073 Å was used for single crystal XRD. The crystal system is orthorhombic and unit cell dimensions are a = 5.5801(12) Å, b = 9.804(3) Å, c = 11.804(3) Å, cell volume V=645.7(3) Å^3 ,α = 90°, β = 90°, γ = 90°. The presence of calcium ions in LACCM doped with calcium chloride was confirmed by EDAX. The composition of the elements present in the Calcium chloride doped LACCM crystals are displayed along with SEM image in Fig. 3 & 4.

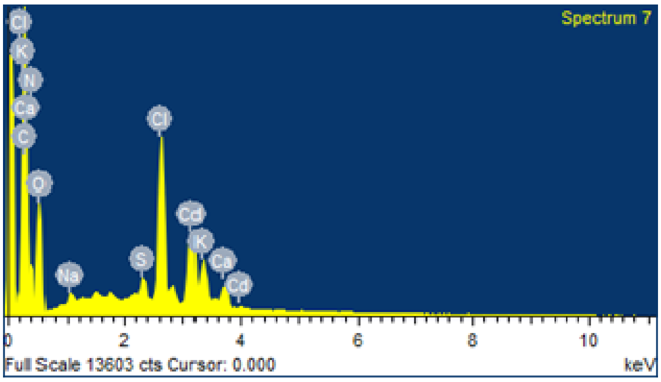

Fig. 4. EDS of 1 mol% $CaCl_2$ doped LACCM crystal

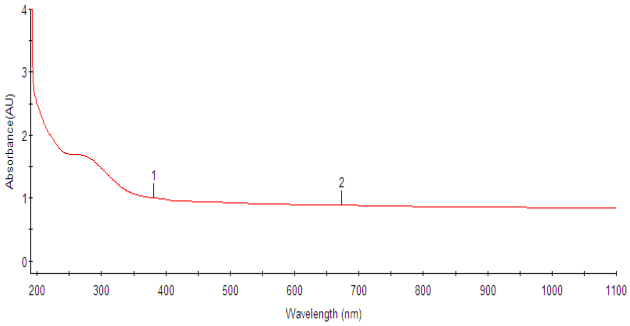

Fig. 5. UV visible spectra $CaCl_2$ doped LACCM crystal

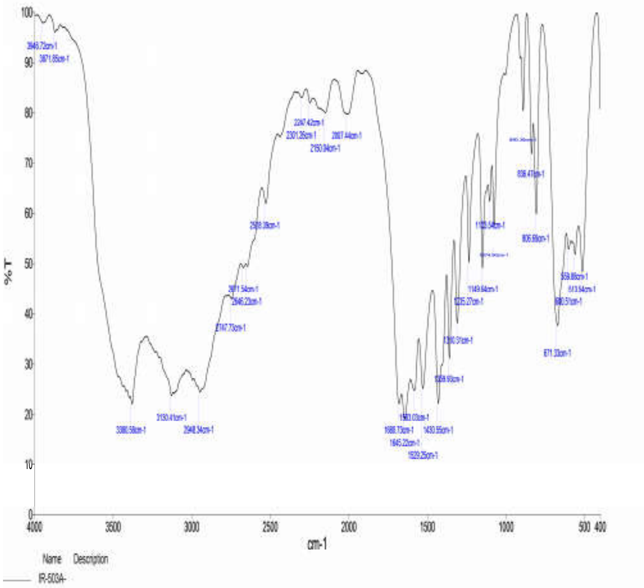

Fig. 6. FTIR spectrum of $CaCl_2$ doped LACCM crystal

UV- visible spectral studies

To determine the optical transmission range, selected optically clear surface of the grown crystal was analyzed by UV visible spectra in the wave length range between 200-1100 nm and it is shown in figure 5. It is observed from the spectra that the calcium chloride ($CaCl_2$) doped LACCM crystal show good transmittance in the entire visible region. As observed in the range 350-700 nm. Hence the crystal can be used for NLO application. The UV cut off wave lengths of the calcium chloride ($CaCl_2$) doped LACC crystals are observed to be 381 nm and 673 nm . In the entire visible region, the optical absorption spectra are flat and constant.

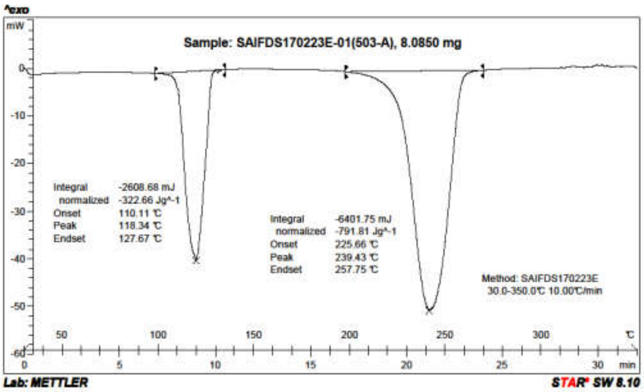

Fig. 7. DSC spectrum of $CaCl_2$ doped LACCM crystal

Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR spectrum of calcium chloride ($CaCl_2$) doped LACCM crystal was recorded in the range of 1000-4000 cm^{-1}. The FTIR spectrum is shown in the fig 6. And the nature of chemical bonding between different functional group are tabulated and given the table.

Table 1. FTIR Assignment for $CaCl_2$ doped LACCM crystal

Wave Number cm^{-1}	Assignments
3380	NH stretching vibration
3130	NH stretching vibration
2948	CH and CH_2 stretching due to NH_2 over lapping
2747	NH stretching vibration
2646	Asymmetric and symmetric stretching mode of NH_2
2671	Asymmetric and symmetric stretching mode of NH_2
2528	O-H and NH stretching
2301	CN stretching vibration
2247	Asymmetric NH_3^+ bending vibration
2150	CN stretching vibration
2007	CS symmetric stretching vibration mode
1680	NH_2 bending vibration
1645	NH_2^+ in plane deformation
1583	Stretching (C=S)
1430	Bending of CH_2
1359	CH_3 symmetric bending and rocking mode
1310	OH plane bending vibration
1235	Rocking of CH_3
1149	Stretching asymmetric and symmetric C-C-N
1103	N-C-N stretching vibration
1074	N-C-N stretching vibration

The peak appearing at 3380,3130 and 2747 cm^{-1} was assigned to the N-H stretching vibration were observed at 2948cm^{-1} ,asymmetric and symmetric stretching modes of NH_2 was observed at 2646 cm^{-1} and 2671 cm^{-1}.OH and NH stretching was observed at 2528 cm^{-1}the peak for the CN stretching vibration was observed at 2301 cm^{-1} and 2150 cm^{-1}. The peak appearing at 2247 cm^{-1}was assigned to the asymmetrical NH_3^+ bending vibration, the CS symmetric stretching vibration mode was observed at 2007 cm^{-1}. The NH_2^+ in plane deformation was observed at 1430 cm^{-1}. The OH plane bending vibration was observed at 1310 $cm^{-1.}$ The peak appearing at 1359cm^{-1} was assigned to the CH_3 symmetric bending ad rocking mode the observed peak at 1235 cm^{-1} were assigned to rocking of CH_3. The peak for the stretching asymmetric C-C-N was observed at 1149 cm^{-1} .the N-C-N stretching vibration was observed at 1074 cm^{-1} and 1103 cm^{-1}. The peak values and their corresponding assignments are given in Table 1.

NLO test

The NLO property of the crystal was confirmed by the Kurtz and Perry powder technique (Kurtz *et al.*, 1968). The transmitted fundamental wave was passed over a monochromator, which separates 532 nm (second harmonic signal) from 1064 nm and absorbed by a $CuSO_4$ solution, which removes the 1064 nm light. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope. The powder SHG efficiency of the crystal is compared with KDP and it is found to be 0.98 times that of KDP due to the higher polarization of smaller ionic radii Ca ions.

Thermal analysis

Thermal stability of calcium chloride doped LACCM crystal was studied by DSC analyses. The recorded DSC spectra of the sample are shown in Fig. 7. From the DSC curve, the thermal stability of the sample is realized upto 400°C. Sodium chloride doped LACCM material shows loss in weight due to the molecules, which are loosely bounded to the central metal atom at 117-130°C and 239- 257 °C. These molecules break their bonds get detached and leave the complex as fragments from the coordinating sphere. Thermal resistance offered by calcium chloride doped LACCM has been observed upto 400 °C, which is attributed to high cohesive energy of the transition metal complex with strong bonding nature (Razzetti *et al.* 2002). The binding energy of ionic crystal (sum of electrostatic and Van der Waal spart of attractive interactions) explains the thermal resistance of the complex. Endothermic peak reveals that melting occurs at 118° C and subsequent exothermic peak represents the decomposition nature of the sample.

Conclusion

The organometallic NLO single crystals of calcium chloride doped L-aspargine cadmium chloride (LACCM) were grown by slow evaporation technique and characterized by X-ray diffraction (single crystal land power) studies. PXRD results revels the crystal system is orthorhombic .The presence of calcium impurity was confirmed by energy dispersive analysis by X-ray. This crystal show good transmittance in the entire visible regionand hence can be used for NLO application. FTIR analysis confirms the presence of functional materials. The NLO property is confirmed by SHG measurement. Thermal analysis shows this crystals are thermally stable upto 400°C.

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