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Synthesis, growth and Characterization of Energy Material

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Abstract : L-Asparagine Cadmium acetate (LACA), a semi organic single crystal was grown from aqueous solution by slow evaporation technique. A good optical quality single crystal of size 17×9×5 mm^3 was grown within period of 4 weeks. The grown crystal was characterized by XRD, FT-IR, TGA-DTA, UV-Vis, dielectric analysis, and NLO studies.
Keywords: L-Asparagine, cadmium acetate, spectral, thermal, optical, NLO

Introduction

In the recent years, efforts have been directed to explore new nonlinear optical materials due to the applications of NLO in the field of laser frequency conversion, optical parametric oscillation, second harmonic generation, optical switching, etc[1-7]. The crystalline salts of optically active amino acids represent an important of semi-organic crystals, which have a wide range of electronic characteristics, mechanical, hardness and thermal stability[8]. Amino acids and their complexes belong to a family of organic materials that have been considered for photonic applications[9].The vaious L-asparagine complexes, L-asparaginium picrate[10], shows high nonlinearity, 66.5 times of KDP crystal. Recently, Natarajan et al reported the crystal structure of L-asparagine L-tartarate compound[11]. In the present study, we report the growth and characterization of L-asparagine cadmium acetate crystal.

Experimental procedure

LACA was synthesized from L-asparagine cadmium acetate taken in the ratio 1:1. The requied quantity of L-asparagine and cadmium acetate was estimated according to the following raction:

The calculated amount of the reactants were thoroughly dissolved in double distilled water and stirrer well for about 5 h using magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution with pH at 5. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation under room temperature. Transparent salt was then purified by repeated in a period of 30 days. The photograph of the grown crystal is shown in Fig.1

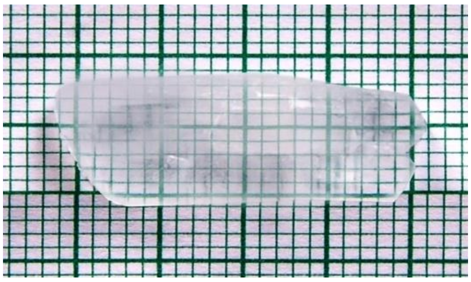

Fig.1Photograph of grown LACA single crystal

Results and discussion

XRD

A Bruker kappa APEXII single crystal X-ray diffractometer with MoKα (λ=0.71073Å) radiation was used to estimate the cell parameters of LACA crystal. The single crystal X-ray diffraction study was carried out to confirm the cell parameters of LACA crystal. The crystal belongs to orthorhombic structure with space group $P2_1P2_1P2_1$. The estimated cell parameters are a= 5.604Å, b= 9.846Å, c= 11.839Å and volume V= 653$Å^3$. In case of L-asparagine cadmium acetate crystal, slight variations in the lattice parameters and cell parameters and cell volume were observed. This variation may be attributed to the incorporation of cadmium acetatein voids space of the L-asparagine monohydrate (LAM). The single crystal X-ray diffraction values of pure LAM[12] and LACA are compared and presented in Table 1.

Table 1. Single crystal XRD data of pure LAM (12) and LAM Cadmium acetate

Crystal parameters	Pure LAM	LAM-cadmium acetate
a (Å)	5.597	5.604
b (Å)	9.819	9.846
c (Å)	11.792	11.839
Volume $(Å)^3$	648.05	653
Crystal System	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$

Fourier Transform Infrared (FTIR) spectroscopic studies

Fourier Transform infrared (FTIR) spectrum has been recorded to analyze the presence of various functional groups. The Fourier transform infrared analysis was carried out between 400 cm^{-1} and 4000 cm^{-1} by recording the spectrum using a Perkin – Elmer spectrometer by KBr pellet technique. The recorded spectrum is shown in Fig (2).

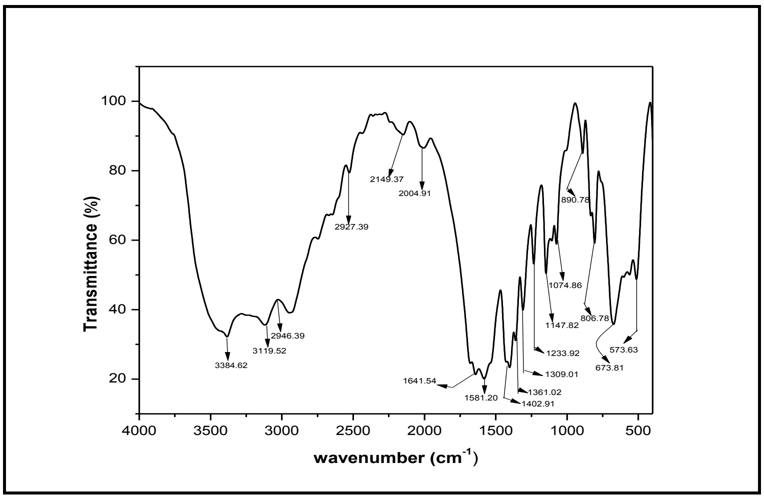

Fig.2 FTIR spectrum of LACA

The intense broad band envelops between 2200 and 3800 cm^{-1} is due to OH stretching. NH stretching and CH_2 symmetry and asymmetry vibrations. In the crystal, there exist extensive hydrogen – bonding interactions whose vibrational frequencies strongly depend on the length of these bonds. The weak hydrogen bonds are characterized by strong, broad, and multicomponent absorption extending into the regions 3227-2354 cm^{-1}, while the strong ones give broad and very strong absorption below 2000 cm^{-1}[113].The fine structure in the lower energy protion of the envelope indicates the hydrogen bonding. The C=O and NH vibration are observed at 1641 cm-1 and 3119 cm-1 respectively. The peaks at 1147 and 1074 cm-1 are assigned due to C-O vibrations of acetate group. The peaks at 1641 cm^{-1} is due to symmetric stretching vibration of C=O. Other Characterization vibration establishing the identify of the compounds are represented in Table 2. The FTIR spectra of both the pure LAM (12), LACA confirm the spectral aspects of pure compounds. Although the spectrum of cadmium acetate, LAM provides similar features as that of pure LAM, there is slight shifting observed that it may be due to the incorporation of cadmium acetate in the lattice of LAM

Table 2. FTIR spectral assignments of pure LAM (12) and LACA

Pure LAM	LAM-cadmium acetate	Vibrational assignment
3447	3384	O-H stretching
-	3119	NH stretching
3382	-	NH_2 stretching
2952	2946	C-H stretching
1528	1581	NH_2 bending
1428	1402	COO^- sym. Stretching
1360	1361	CH bending
1314	1309	CH_2 wagging
1235	-	NH_2 rocking
1149	1147	NH^{3+} rocking
1074	1074	C-N stretching
910	890	CH_2 rocking
807	806	C-C stretching
666	673	H_2O rocking
511	513	C-N torsion

Optical transmittance studies

The UV-Vis transmission spectrum of LACA crystal was recorded with Lamda 35 spectrometer in the range 190-900 nm and the recorded spectrum is shown in Fig.(3).The transmittance spectrum of pure LAM and LACA crystal. The lower cut-off wavelength is found to be at 230nm. The transmission spectrum shows that the crystal has wide transmittance of about 45% up to 900 nm which will be useful for nonlinear optical device applications. The transparent improved compare with pure LAM (12)

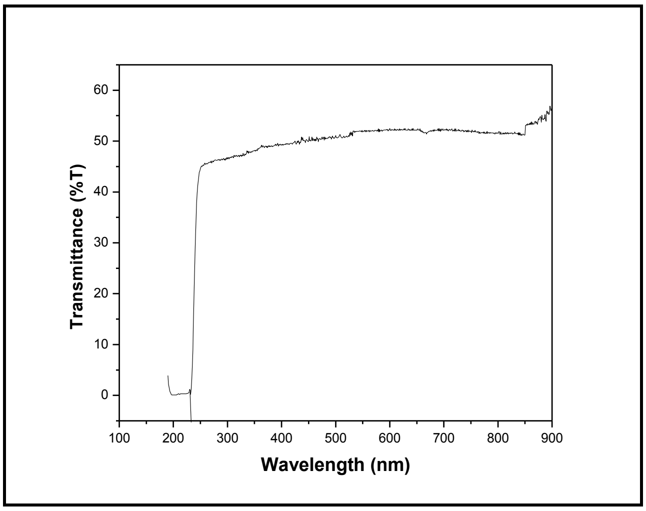

Fig.3UV-Vis spectrum of LACA

Dielectric studies

The dielectric constant is one of the basic electrical properties of solids. Studies of the temperature and frequency dependence of dielectric properties unveil useful information about structural changes, defect behavior and transport phenomena[14]. Dielectric studies were carried out on the LACA crystal sample for 120°C frequencies at room temperature. The dielectric experiment was performed in the frequency range 100 Hz – 6 MHz. The dielectric constant ε_r and dielectric loss were estimated using the relation

$\varepsilon_r = Ct / \varepsilon_\circ A$, and
$\tan\delta = \varepsilon_r D$

Where C is the capacitance, t is the thickness of the crystal, $\varepsilon_\circ$ is the permittivity, D is the dissipation factor and A is the area of the cross section of crystal sample. The dielectric constant and dielectric loss versus frequency were plotted as shown in Fig (4) & (5). The dielectric constant as a function of both frequency and temperature was measured and it is observed that dielectric constant decreases with increase in frequency, which is usually referred to as anomalous dielectric dispersion[15]. According to the Miller rule[16], lower value of dielectric constant will be suitable for the enhancement of SHG efficiency.

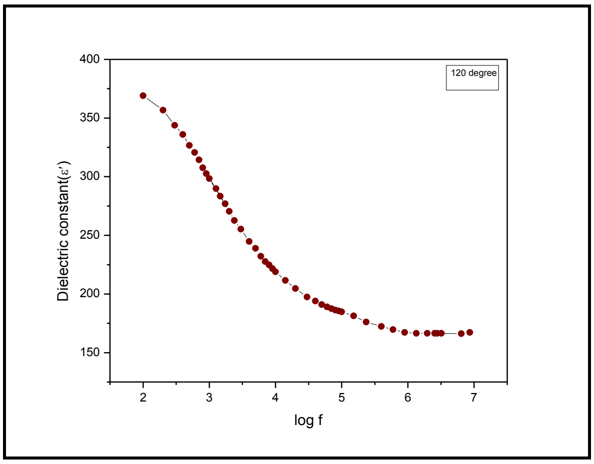

Fig. 4 Variation of Dielectric constant with frequency

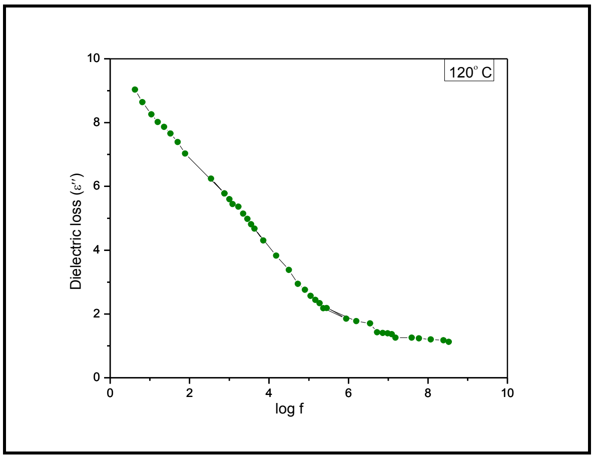

Fig. 5Plot of Dielectric loss versus logfrequency

The larger value of dielectric constant at low frequency enumerates that there is contribution from all four known sources of polarization is generally active at lower frequencies and high space change polarizations. Space charge polarization is generally active at lower frequencies and high temperatures. The changes in ε_r and tanδ as a function of frequency for LACA may be considered as a normal behavior of dielectric. The low value of dielectric loss indicates that the grown crystal of LACA is of reasonably good quality.The alternatingcurrent conductivity σ_{ac} (Ω^{-1} m^{-1}) is calculated usingtherelation

$\sigma_{ac} = 2\pi f\, \varepsilon_0 \varepsilon' \tan\delta$

Where f is the frequency of the appliedac field (Hz).The frequency variation of the ac conductivity at different temperatures for the given sample in temperature range 120°C areshownin Fig.(6). The acconductivity patterns show frequency independent plate auinthelow frequency regionand exhibits dispersion at higher frequencies[18]. The trend indicates that the electrical conductivity will increase greatly during the relaxation process at increased temperature.

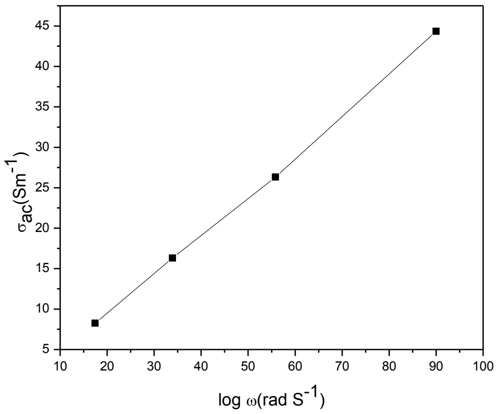

Fig.6 Variation of log ω(rad S^{-1}) Vs conductivity

Thermal studies

To know the thermal stability of the grown crystal, powder sample of the specimen was subjected to thermal analysis to find out the weight loss (TG) and energy change (DTA) in the sample with respect t in the sample with respect to the temperature range from 30 to 1000°C in an alumina crucible in the nitrogen atmosphere using SDTQ 600V8.3Build101instrumentataheatingrateof 20°C/min. The TG and DTA curves are shown in Fig (7). In TGA, there is no weight loss up to 20°. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. The pure LAM crystal, the TGA curves shows there stages of weight loss. The first stage (between 102 and 207°C) is about 11% due to the evaporation of absorbed water. The second stage is between 207 and 250°C and the third stage is between 258 and 290°C with a weight loss of 24 % and 38 % due to the libration of volatile substances. From the DTA curve, there is sharp endothermic peaks at 113.45°C is showing the thermal stability of the LAM crystal. But the LACA was seen that the major weight loss (around 11.64 %) states at 175°C and it is continues up to 420°C the residual mass 17.84% (999.8°C). However, above this temperature, no weight loss has been observed, In the DTA, the strong exothermic peaks located at ~200°C, 225°C, 275°C depict the crystallization of some the phase of the decomposed material, The DTA curve, there is sharp exothermic peaks at 275°C showing the thermal stability of the LACA crystal.

Nonlinear optical studies

Nonlinear optical properties of the grown LACA crystal studied by Kurtz and Perry power technique (17). A Q-switched Nd-YAG laser was used as light source. A laser beam of fundamental wavelength 1064 nm with 8 ns pulse width and 10 Hz pulse rate was made to fall normally on the crystal sample cell. Potassium dihydrogen phosphate (KDP) crystal was used as reference material in the SHG measurement. The input laser energy incident on the powdered sample was chosen to be 5.9 mJ/pluse. The intense second harmonic signal was observed from LACA crystal and the SHG signal was found to be 0.7 times that of KDP crystals. The second harmonic generation (SHG) studies of Pure LAM and LACA are presented in Table 3.

Table 3. Second harmonic generation (SHG) studies of Pure LAM (12) and LACA

SHG studies	Pure LAM	LACA
Technique	Kutz and perry	Kutz and perry
Laser source	Nd-YAG laser	Nd-YAG laser
Wavelength	1064 nm	1064 nm
Pulse with	8 ns	8 ns
Pulse rate	10 Hz	10 Hz
Input laser energy	0.5 J	0.68 J
Output energy	2.7 mJ	5.9 mJ

Conclusion

Single crystal of LACA was grown by slow evaporation technique in a period of 30 days. X-ray diffraction studies confirm the crystallinity and shows that LACA crystal is Orthorhombic in the structure belonging to $P2_12_12_1$ space group. The UV-Vis spectra confirm the crystal is transparent in the range of 190-900 nm. The dielectric studies revealed that the grown crystal has low dielectric constant with less power dissipation and hence this crystal can be used for electro-optic applications. The thermal behavior of the grown crystal was studied by using TG-DTA method. Kurtz and Perry powder technique revealed the second order nonlinear optical property of LACA crystal.

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