

DIELECTRIC STUDIES ON NOVEL ORGANOMETALLIC NLO SINGLE CRYSTAL: L-ASPARGINE CADMIUM CHLORIDE MONOHYDRATE (LACCM)

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Abstract

Single crystals of L-asparagine cadmium chloride (LACCM), an organometallic non linear optical material, have been grown by the slow evaporation technique. The grown crystals were subjected to various characterization techniques, such as single crystal and powder XRD, FTIR. Electrical parameters, such as dielectric constant, dielectric loss, ac and dc conductivity and their corresponding activation energies have been studied. The low dielectric constant and dielectric loss suggest that this material is a good candidate for micro-electronic applications.

Key words: Crystal growth, Thermal properties, Optical materials and properties, Dc conductivity Dielectric properties,

1.Introduction

Materials with high second order non-linear effect, wide transparency, stable physio-chemical performance, high resistance to laser damage threshold and large size crystal have been widely investigated for device applications in the field of optoelectronics, optical data storage and frequency conversion [1-4]. The search of highly efficient second order non-linear optical (NLO) materials has resulted in organometallic materials show good thermal stability and wide optical transmittance composed to organic materials and the mechanical behavior has been improved compared to inorganic materials, when inorganic distorted polyhedra bond with organic chromophores[5]. Organometallic compounds differ from most organic NLO materials by charge transfer transitions i.e metal-to-ligand and ligand-to-metal. These NLO metal complexes exhibit donor (π -conjugate bridge) and acceptor (D- π -A) structures [6].

In case of metal organic co-ordination complexes the organic ligand is usually more dominant in the nonlinear optical (NLO) and dielectric effects, The metallic part focus in on group II B metals (Zn, Cd and Hg). These compounds usually have high transparency in UV region, because of their closed d^{10} shell. Potential NLO materials like bis thiourea cadmium chloride (BTCC), triallyl-thiourea cadmium chloride (TATCC)[7] are examples of this approach.

The amino acids are the famous organic materials. Play a vital role in the field of nonlinear optical crystal growth. Many members of natural amino acids individually exhibiting the nonlinear optical properties because they have a donor NH_2 and acceptor $COOH$ group and the intermolecular charge transfer is also possible. Especially natural amino acids such as Arginine, alanine, lysine and γ glycine are evidently showing NLO property because of additional $COOH$ group in first and NH_2 group in second. Therefore mixing of amino acid with already known organic, inorganic or semi-organic NLO materials may improve their NLO and ferroelectric properties. The literature survey confirmed the studies on improved second harmonic generation, thermal, and opto-electric properties of crystals grown by mixing equimolar ratios of amino acids L-alanine, L-arginine with malic acid, oxalic acid and nitric acid and acetic acid [8-12]. Usha et

al.[13] reported that the comparatively high optical nonlinearity comes from the distortion of the tetrahedron, which is composed of three allyl thiourea and one Cl or Br combining with the metal atoms Cd^{2+} or Hg^{2+} . The distorted tetrahedron arrangement in the material increases the asymmetric structure and hence contributes to the enhanced NLO activity. A few authors have reported about this material [14-16]. In our present work the single crystals of LACCM were grown by slow evaporation technique and characterized. The result FTIR, XRD analysis and electrical studies of the grown crystals are reported.

2.Experimental Procedure

The LACCM crystals were synthesized from L-asparagine and cadmium chloride monohydrate in the equimolar ratio. The calculated amounts 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. Supersaturated aqueous solution was 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. The temperature and volume were kept constant, respectively at 30°C and 20ml for all the crystal growth experiments. Small crystals appeared in the beginning due to slow evaporation and grew larger (up to about 2 cm in size) in considerable finite time of about 6 hrs. After the completion of growth, crystals were harvested. Good quality optically transparent large size crystals were selected for carrying out the measurements.

FTIR studies of the grown crystals were analyzed by Fourier Transform Infra Red spectrometer model SPECTRUM RXI make PERKIN. 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 $\text{MoK}\alpha$ ($\lambda = 0.717 \text{ \AA}$) radiation. Powder X-ray spectrum was obtained by PANalytical X'Pert Pro Powder X'Cellerator Diffractometer. The temperature dependent capacitance (C) and dielectric loss factor ($\tan \delta$) measurements were carried out on the prepared crystals with an accuracy of $\pm 1 \%$ with APLAB LCR Meter in the temperature range of $40 - 150^\circ\text{C}$ at 100 Hz and 1kHz frequency. The observations were made while cooling the sample by using the conventional two-probe technique [17,18]. Temperature was controlled to an accuracy level of $\pm 1^\circ\text{C}$. The air capacitance (C_{air}) in between the two electrodes was also measured.

3.Results and discussion

Crystals with regular shape and size of about $14 \times 11 \times 5 \text{ mm}^3$ were harvested within 20 days. The photograph of the grown LACCM crystals is displayed in Fig. 1. The external appearance or morphology of the grown crystals seems to be polyhedron in shape. 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.

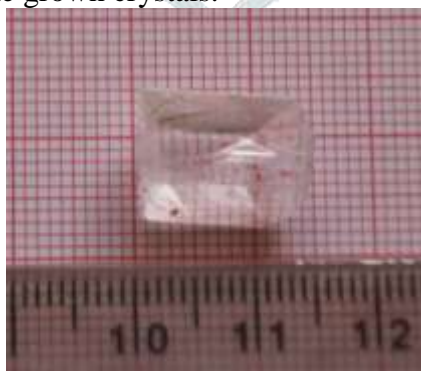


Fig. 1 : The photograph of grown LACCM crystal

The formation of functional groups was confirmed by using SPECTRUM RXI make PERKIN FTIR spectrometer by KBr pellet technique with a scan range of $4000 - 400 \text{ cm}^{-1}$ as shown in Fig. 2. The peak around $3384.02 - 3112.00 \text{ cm}^{-1}$ is due to NH stretching of NH_2 vibration. The peak obtained at 2992.79

cm^{-1} is due to CH_2 vibration of the amino acid. The $\text{NH}_3 +$ asymmetric vibration is observed at 1644.46 cm^{-1} and NH_2 torsional oscillation at 513 cm^{-1} . The peaks obtained at 1529.36 and 1430.43 cm^{-1} are due to asymmetric and symmetric vibrations of COO^- [19]. The C-C-COO vibration occurs at 1236.12 and 1150.45 cm^{-1} . The peak obtained at 891.11 cm^{-1} is due to C-C-N symmetric vibration. The peaks at 668.94 and 514.82 cm^{-1} indicates that COO^- bending and COO^- rocking vibration. These vibrations proved the presence of expected functional groups in the synthesized compound.

Crushed powder of LACCM crystal was subjected to powder X-ray diffraction analysis. The sample was scanned the wide range of $0-80^\circ$ with a scan rate of $2^\circ/\text{min}$. The recorded X-ray pattern of LACCM is shown Fig 3. The prominent well defined sharp Bragg's peak at specific 2θ angle reveals that the good crystalline nature of LACC crystal. Crystal size of $0.200 \times 0.200 \times 0.300 \text{ mm}$ and wave length 0.71073 \AA was used for SCXRD. The crystal system is orthorhombic and data obtained is tabulated in table 1. The SEM studies gives information about surface morphology in the grown crystals. The surface features of the crystal was observed by a scanning electron microscopy in figure 4 shows the obtained micrograph, it is observed that the growth surface shows the spherical shaped atoms. Elemental analysis was carried out for LHFBB by the energy dispersive X- ray analysis to confirm the composition of these elements.

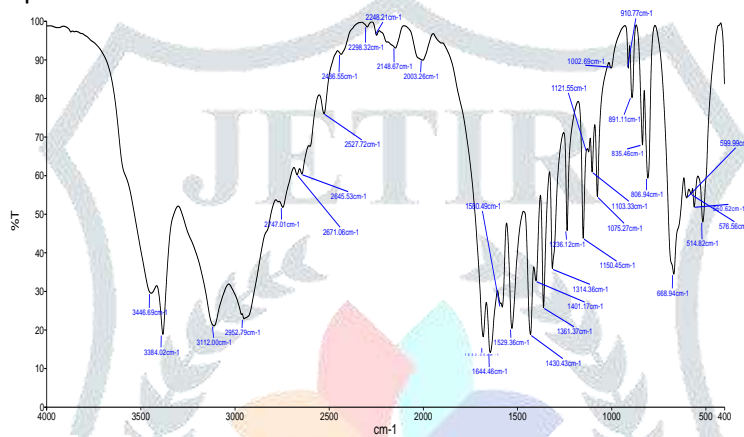


Fig. 2: FTIR spectrum of LACCM crystal

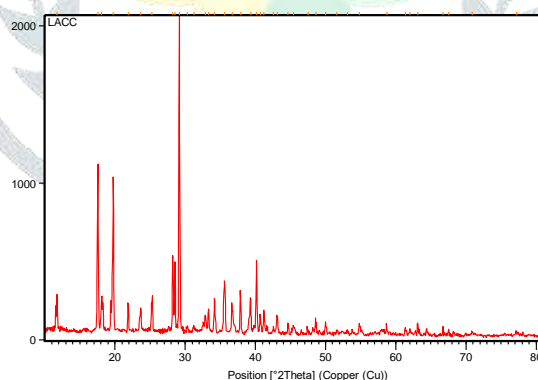


Fig. 3: XRD pattern of LACCM crystal

Table 1. Sample and crystal data for LACCM_

Crystal system	orthorhombic	
Unit cell dimensions	$a = 5.5777(19) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 9.820(2) \text{ \AA}$	$\beta = 90^\circ$
	$c = 11.795(2) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$646.1(3) \text{ \AA}^3$	

AC conductivity measurements

The sample crystals cleaved perpendicular to the polar axis with thickness about 4 mm having graphite coating on the opposite faces were used for dielectric measurements. The flat surfaces of the crystals were coated with good quality graphite to obtain a good conductive surface layer. Using a traveling microscope the dimensions of the pellets were measured. The capacitance (C_c) and the dielectric loss factor ($\tan \delta$) were measured using the conventional parallel plate capacitor method [4,23] using an LCR meter (APLAB MODEL 4912) for all the samples with two frequencies 100 Hz and 1 kHz at various temperatures in the range 40 – 150°C. The observations were made while cooling the sample [20]. The temperature was controlled to an accuracy of $\pm 1^\circ\text{C}$. Air capacitance (C_a) was also measured for the thickness equal to that of the pellet. The area of the pellet in contact with the electrode was same as that of the electrode. The air capacitance was measured only at room temperature because the variation of air capacitance with temperature was found to be negligible. The dielectric constant of the pellet sample was calculated using the relation,

$$\epsilon_r = C_c / C_a.$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta.$$

Here, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency).

DC Conductivity Measurements

The DC electrical conductivity measurements were carried out to an accuracy of $\pm 3\%$ using the conventional two-probe (parallel plate capacitor) technique at various temperatures in the range 40–150 °C [1,24]. The sample was prepared as done for the AC conductivity measurement. The resistance of the sample was measured using a million megohmmeter. The observations were made while cooling the sample. Temperature was controlled to an accuracy of $\pm 1^\circ\text{C}$. The dimensions of the sample were measured using a traveling microscope (least count = 0.001 cm). The DC conductivity, σ_{dc} , of the crystal was calculated using the relation

$$\sigma_{dc} = d/(RA)$$

where R is the measured resistance, d is the thickness of the sample, and A is the area of the face in contact with the electrode.

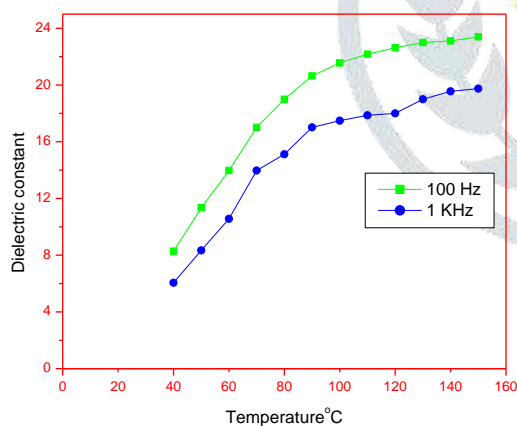


Fig. 4: Variation of dielectric constant with temperature of LACCM crystal

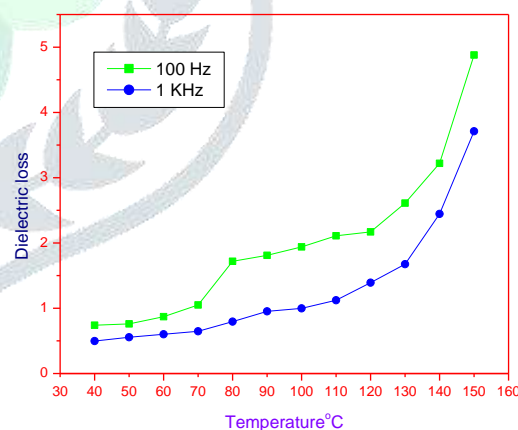


Fig. 5: Variation of dielectric loss with temperature of LACCM crystal

Dielectric constant of a solid material depends on the presence of atoms and molecules and their arrangements [21]. The σ_{ac} , ϵ_r , σ_{dc} and $\tan \delta$ values obtained are, within experimental error, the same and shown in fig. 4-7. It can be seen that the σ_{dc} , ϵ_r , $\tan \delta$ and σ_{ac} values increase with the increase in temperature. The increase of conductivity with the increase in temperature observed in the present study is similar to that observed for some organic impurities (like samarium tetratrate, L-arginine, urea, and thiourea). [22-24].

Electrical conductivity of the NLO crystals is determined by the proton transport within the framework of hydrogen bonds [25]. Two mechanisms can be considered: the first one is identical to the conductivity mechanism in ice also containing hydrogen bonds [26]; according to the second mechanism, conductivity is associated with the incorporation into the crystal lattice of impurities having different valences and the formation of corresponding defects in ionic crystals. It is assumed that the conductivity of ice is determined by the simultaneous presence of positive and negative ions and orientational defects-vacant hydrogen bonds (L-defects) and doubly occupied hydrogen bonds (D-defects). Other possible defects are vacancies and defect associates [27]. The experimental data and especially the character of the temperature dependence of conductivity allow us to state that the conductivity of ADP crystals is determined by both thermally generated L-defects and the foreign impurities incorporated into the lattice and generating L-defects there [28]. From the above knowledge, it is understood that the proton transport depends on the generation of L-defects. Hence, the increase of conductivity with the increase in temperature observed LACCM crystals in the present study can be understood as due to the temperature dependence of the proton transport.

It is a known fact that cadmium chloride is a model ionic substance, and it may exist as ions in the crystals. So, the Cl⁻ ion is expected to move (in all directions) along with protonic movement. From this it can be understood that the movement of Cl⁻ also contributes significantly to the electrical conductivity of LACCM single crystals. This explains the greater temperature dependence of electrical conductivity observed in the case of LACCM crystals. The conductivity increases smoothly through the temperature range considered in the present study; there is no sharp increase that would be characteristic of a superprotonic phase transition [29]. This behavior is entirely in agreement with the reported tetragonal structure of ADP. In addition, it should be noted that the σ_{dc} values are more than the σ_{ac} values at all temperatures. This is similar to that observed for L-arginine based crystals [30]. The reason for this is not understood at present. However, it may be mentioned that when AC voltage is applied, some obstruction is given by the natural impurities in random directions which may cause the reduction in AC conductivity.

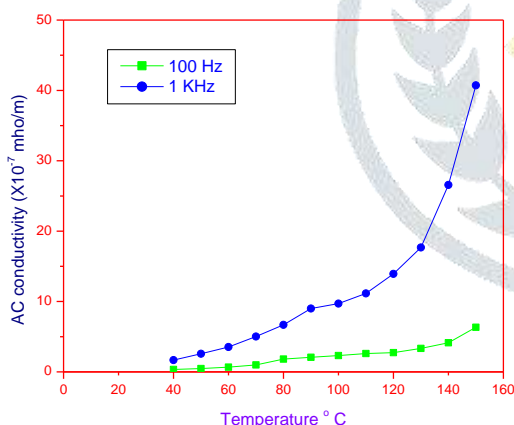


Fig. 13: Variation of AC conductivity with temperature of LACCM crystal

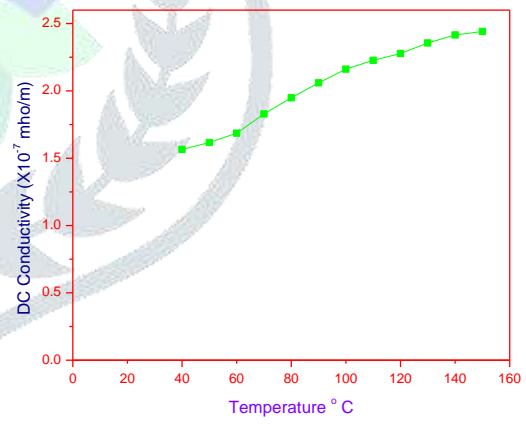


Fig. 14: Variation of DC conductivity with temperature of LACCM crystal

The increase of dielectric constant and dielectric loss factor with the increase in temperature observed for LACCM crystals in the present study is similar to that observed for amino acid added crystals [31,32]. Plots between $\ln \sigma_{dc}$ and $1000/T$ and $\ln \sigma_{ac}$ and $1000/T$ (not shown here) are found to be nearly linear. So, the conductivity (both DC and AC) values were fitted to the Arrhenius relations,

$$\sigma_{dc} = \sigma_{odc} \exp[-E_{dc}/(kT)] \quad \text{and} \quad (2)$$

$$\sigma_{ac} = \sigma_{oac} \exp[-E_{ac}/(kT)] \quad (3)$$

where σ_{odc} and σ_{oac} are the proportionality constants (considered to be the characteristic constants of the material), k is the Boltzmann constant, and T is the absolute temperature. The activation energies (E_{dc} and E_{ac}) were estimated using the slopes of the corresponding line plots.

Table 2. Activation energies for LACCM single crystals.

	Activation energy (ev)
E_{ac} at 100Hz	0.4690
E_{ac} at 1KHz	0.6195
E_{dc}	0.2744

The E_{dc} and E_{ac} values obtained in the present study are provided in Table 2. The low activation energies observed suggest that oxygen vacancies may also be responsible for conduction in the temperature region considered in the present study. Both E_{dc} and E_{ac} values are also found to vary as in the case of other electrical parameters.

4. Conclusion

The single crystals of organometallic L-asparagine cadmium chloride (LACCM) were grown by slow evaporation technique and characterized by X-ray diffraction (single crystal and powder) studies. The FT-IR spectral analysis confirms the presence of functional groups in the compound. The low dielectric constant and dielectric loss at high frequency suggest that it is a good candidate for micro-electronic applications.

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