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Growth and characterization of Urea Lead nitrate (ULN) single crystal by slow evaporation process

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ABSTRACT

Semi-organic single crystals of Urea Lead nitrate (ULN) was synthesized by slow solvent evaporation technique. The grown crystals were subjected to different characterizations such as single crystal XRD, FTIR, UV, solubility test, Dielectric and TG-DTA studies. The grown crystals were characterized using single crystal X-ray diffraction analysis, which shows that the ULN crystals are belongs to hexagonal system. From the absorption spectrum, the optical band gap energy is found to be 4.32 eV. The low value of dielectric loss (ε_r) at high frequencies suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications.

Keywords: ULN; Semi-organic crystal; Slow evaporation process; Optical properties; Dielectric studies.

INTRODUCTION

Urea or carbamide is an organic compound with the chemical formula $(NH_2)_2CO$. The molecule has two amide (—NH_2) groups joined by a carbonyl (C=O) functional group. It is highly soluble in water and non-toxic. It is one of the simplest biological molecule and one of the simplest diamide used in organic chemistry because of its capability in forming transition metal complexes. It has shown interesting properties for nonlinear optical applications. Its optical and mechanical properties are comparable to those of semiorganic NLO crystals [1-4]. Lead (II) nitrate is an inorganic compound with the chemical formula $Pb(NO_3)_2$. It commonly occurs as a colourless crystal or white powder and, unlike most other lead (II) salts, is soluble in water.

In the previous reports, the growth of urea and its derivatives like most organic materials is problematic owing to its polar electrical characteristics, which enhance the interaction between

growth surfaces and molecules of solvent and solute. For that reason they usually show irregular growth habits [4]. Hence in order to get better growth habit we have tried to grow the semi-organic crystals of urea lead nitrate (ULN) compound is formed from the strongly organic compound of urea and inorganic compound of lead nitrate and thus the resultant crystal possesses both optical as well electrical properties.

MATERIALS AND METHODS

Equimolar amount of urea and lead nitrate were taken in a beaker contains doubly deionized water, the formation of urea lead nitrate (ULN) is expressed as below:

$$CH_4N_2O + Pb(NO_3)_2 \xrightarrow{H_2O} [(CH_4N_2O)\ Pb(NO_3)_2\ ]$$

In our present study, ULN crystals are grown at room temperature by slow evaporation technique by dissolving 6.6g of urea and 33.2g of lead nirtrate in 100 ml of deionized water under magnetic stirring. The temperature was maintained around 35°C to avoid any decomposition of element from the compound. The pH of the solution was measured to be three. After two weeks, the grown crystals were too small because the evaporation rate is slow. Again, the crystals were recrystallised and filtered; pH was measured and found to be two. A colorless, transparent crystal is obtained. The transparent crystal becomes opaque after two weeks. The photograph of the as-grown crystal is presented in Fig.1.

Fig. 1. As grown crystal of Urea Lead Nitrate.

2.1 Solubility study

Fig.2 shows the solubility curve of ULN single crystal. The purity of the synthesized salt was improved by successive recrystallization process. The solubility was determined for four different temperatures 30, 35, 40 and 45°C by dissolving the solute in deionized water in an airtight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically [5, 6]. The solubility is found to increase with increase in temperature for ULN crystals.

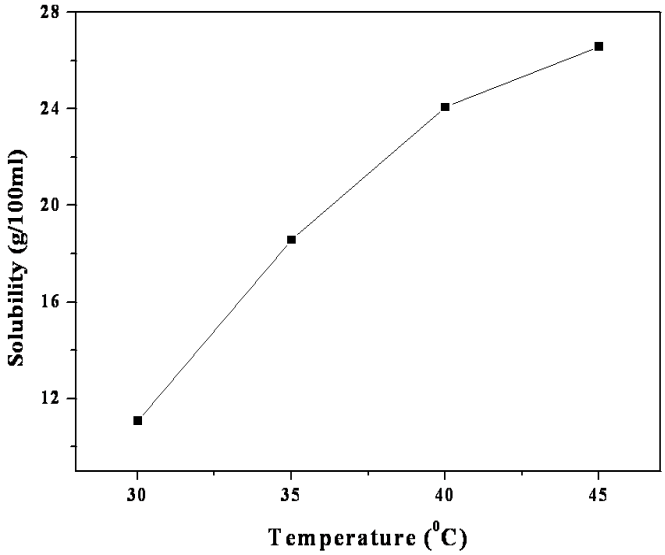

Fig. 2. Solubility curve of ULN.

2.2 Characterization

The single crystal X-ray diffraction study of ULN single crystals was carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer. Fourier transform infrared (FTIR) spectrum of ULN crystal was recorded at a resolution 2 cm^{-1} in the range 400–4000 cm^{-1} employing Bruker IFS-66V spectrophotometer using KBr-pellet technique. The optical absorption spectra of ULN crystals were recorded in the range 200 – 2000 nm using Varian Cary 5E spectrophotometer. Thermal stability and physiochemical changes of the sample were analyzed by recording the TGA and DTA spectrum (TGA Q500 V20.10 Build 36 thermal analyzer) in the temperature range 34–791°C in nitrogen atmosphere at a heating rate of 20°C/min. The temperature dependent dielectric constant and dielectric loss of ULN crystal was measured using HIOKI 3532 LCR HITESTER in the frequency range 50 Hz –5 MHz. In order to ensure good electrical contact between the crystal and the electrodes, a sample of cross-sectional area 24.053 mm^2 and thickness 3.34 mm was coated with silver paint.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis of ULN crystal was carried using an X-ray diffractometer, and the calculated lattice parameter values are a= b=11.06Å, c= 13.56 Å. The studies further reveal, ULN has hexagonal structure and space group is $Pbn2_1$. The Lattice parameter value of ULN single crystals are listed in the table 1.

Table 1: Lattice parameters of ULN crystal

Sample	Lattice Parameters						
	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)
ULN	11.06	11.06	13.56	90.00	90.00	120.00	1437

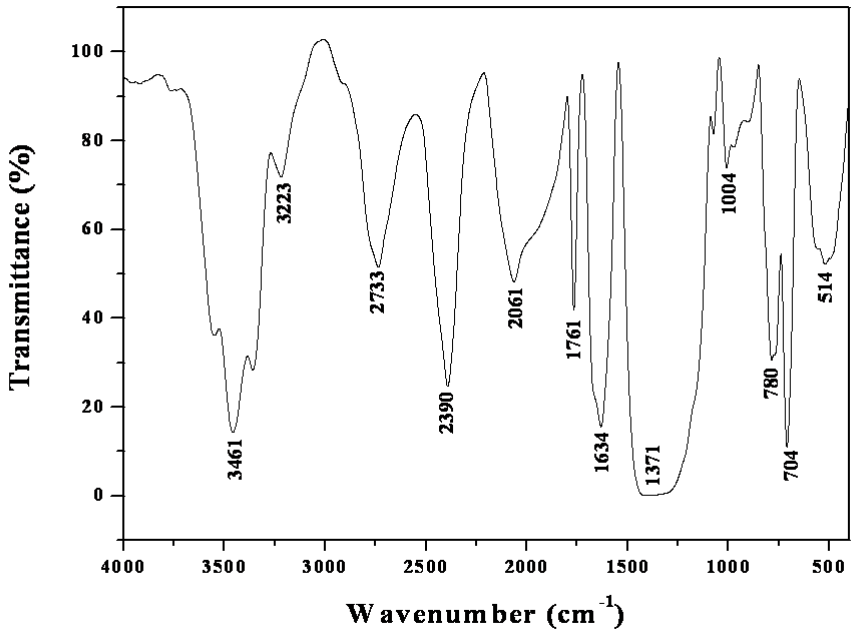

Fig. 3. FTIR spectrum of ULN.

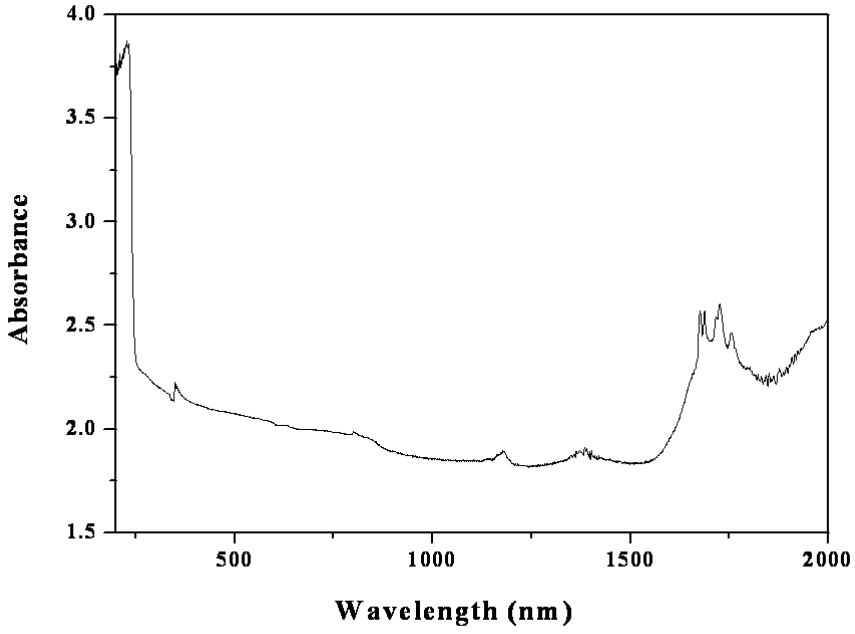

Fig. 4. UV absorption spectrum of ULN.

Fig.3 shows the FTIR spectrum of ULN crystal. The band at 3461 cm^{-1} clearly indicates O-H stretching and the presence of hydrogen bonding and water molecule in the crystal lattice. Sharp peaks near 3223 cm^{-1} and 2733 cm^{-1} are due to symmetric stretching bands of N-H and C-H in the compound, respectively. The C = O stretch of carbonyl groups displays its characteristic peak

at 1761cm^{-1}. The strong band at 1634 cm^{-1} corresponds to NH_3^+ asymmetric deformation and that at 780 corresponds to rocking NH_2. The band appearing at 704 cm^{-1} infers the C-O-H stretching of the ULN crystals. The peak due to the torsional NH oscillations of NH_3^+ is observed at 514 cm^{-1}. Moreover, the presence of very strong and broad absorption band at 1371cm^{-1} can be attributed to the lead nitrate ($Pb(NO_3)_2$) stretching [7,8]**.**

Fig.4 shows the UV absorption spectrum of ULN crystal. The absorbance is found to be very low in the entire visible and near IR region which is the most desired property for the materials possessing SHG. From the obtained spectrum, UV cut-off wave length is found to be 287 nm for ULN crystals. The large transmission in the visible region enables it to be a potential candidate for optoelectronic applications [6]. Using the recorded absorbance (A)–wavelength (λ) data of the crystal of thickness 1mm, absorption coefficient (α) is calculated using the relation,

$$\alpha = (2.303/t).\ \log\ (1/T)$$

where t is the sample thickness and log (1/T) is defined as absorbance (A) of the sample. The value of α is used to determine the optical energy band gap from Tauc's relation [12]. By plotting graph of $(\alpha h\nu)^2$ versus hν as shown in Fig. 5, it is possible to determine the direct band gap, for the crystal. The band gap is obtained by extrapolating the linear part of the curve to the zero of the ordinate and for ULN, the obtained optical energy gap is 4.32 eV.

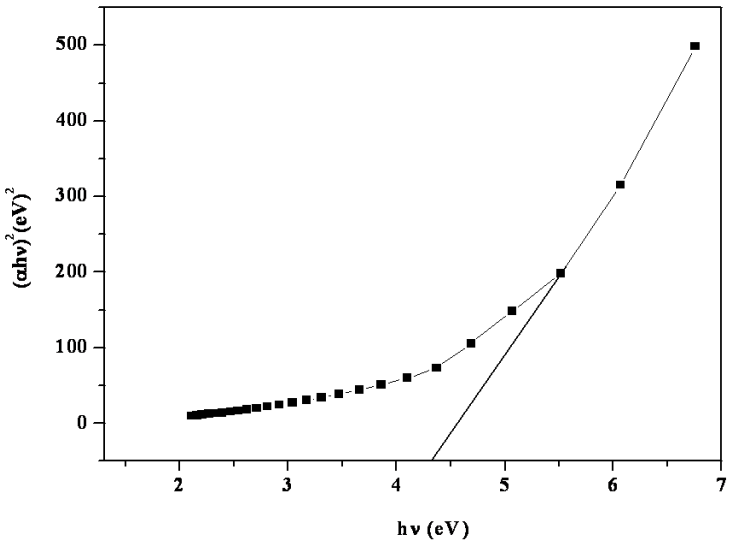

Fig. 5. Plot of $(\alpha h\nu)^2$ versus hν of ULN.

Figure 6 shows the TGA and DTA thermogram of ULN. The compound begins to decompose at 458.7°C and complete decomposition takes place at 527.4°C. Further, from the studies it is observed from the graph that the ULN crystal is thermally stable till 527.4^{o}C after this the sample undergoes appreciable weight loss up to 26.4%. The weight loss corresponds to 35.2% and no residue remains. The change in weight loss confirms the decomposition nature of the sample. The endothermic peaks of the DTA trace coincide with the decomposition in the TGA trace.

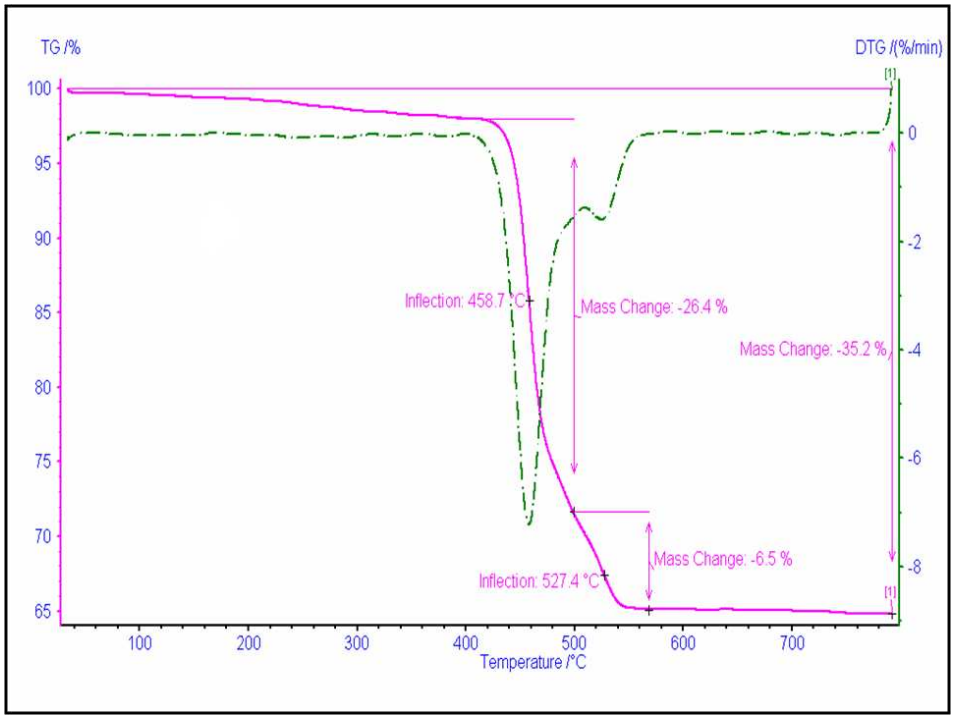

Fig. 6. TGA and DTA thermogram of ULN crystal.

3.1 Dielectric studies

Fig. 7a and 7b show the variations of dielectric constant and dielectric loss of ULN crystal at different temperatures ranging from 40 to 250°C, as a function of frequency. From Fig. 7a it is seen that the value of dielectric constant is found to increase with temperature and it becomes independent of frequency at higher frequency region. The decrease in dielectric constant of ULN crystal at low frequencies may be attributed to the contribution of the electronic, ionic, orientation and space charge polarizations which depend on the frequencies. At low frequencies, all the four contributions are active. As the frequency increases, it is found that the dielectric constant decreases exponentially and it attains a lower value. The dielectric constant is low at lower temperature and it is increases with the increase of temperature sharply up to the Curie point. The dielectric constant of the crystal can be calculated using the equation as follow,

$$\varepsilon_r = Cd/A\varepsilon_o \qquad (1)$$

where d is the thickness of the sample, A is the area of the sample, C is the capacitance of the sample, ε_o is the permittivity of free space and ε_r is the dielectric constant of the sample. The low value of dielectric loss (ε_r) at high frequencies suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications [10].

The DC conductivity (σ_{dc}) of the crystal was calculated using the relation,

$$\sigma_{dc} = d/ AR_{dc} \qquad (2)$$

where, R_{dc} is the total electrical resistance of the sample. The value of R_{dc} is evaluated from the cole-cole plot shown in Fig.7c, between $Z^1 = Z \cos \theta$ (real part of impedance) and $Z^{11} = Z \sin \theta$

(imaginary part of impedance). The electrical conductivity of the as grown crystal at room temperature is found to be 1.26 x 10^{-5} $mhom^{-1}$. The crystal has a low electrical conductivity which is due to the decrease in mobility of the charge carriers and also it brings changes in the electronic band structure. Electrical conduction is observed in the crystal, as a result of electrons jump from metal ions of lead with low valence state to high valence state.

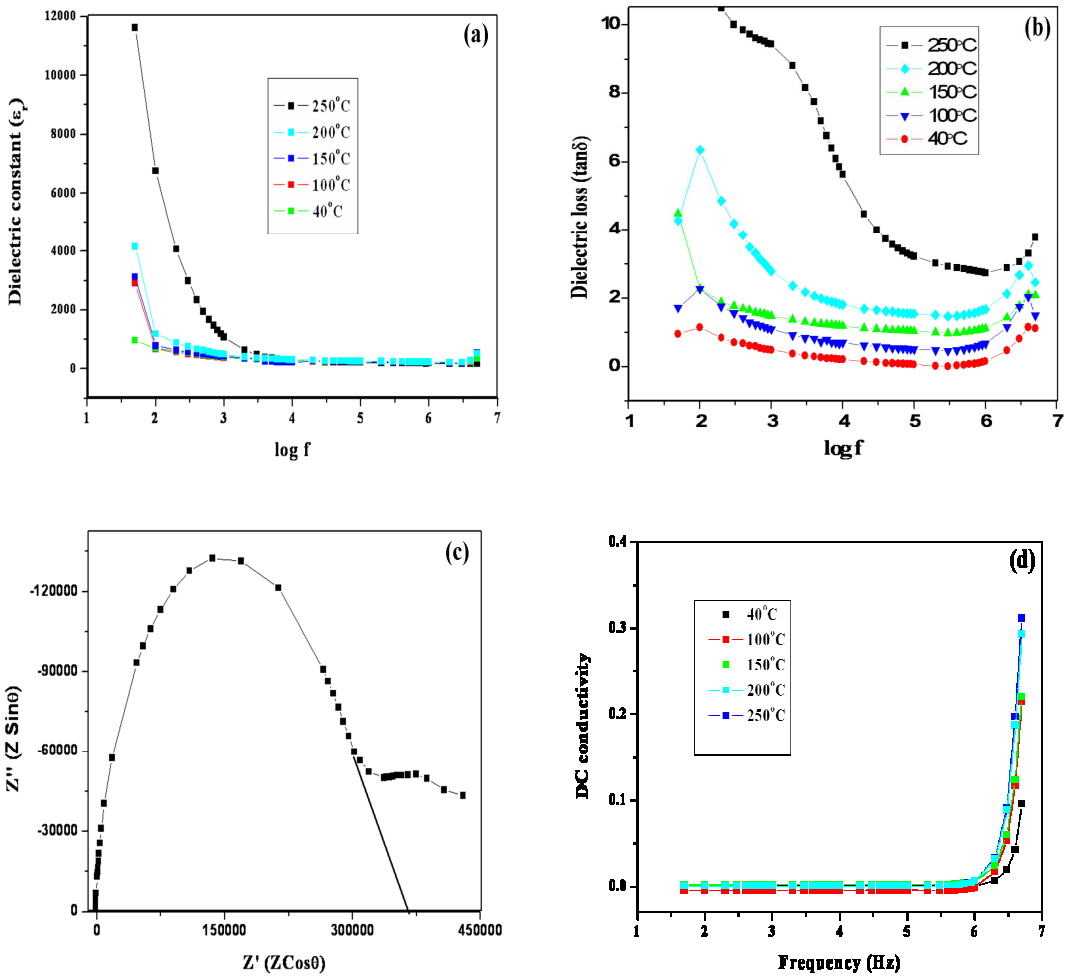

Fig. 7. (a) Variation of dielectric constant Vs frequency, (b) Dielectric loss Vs frequency, (c) Cole–Cole plot between complex impedances for ULN single crystals and (d) Variation of DC electrical conductivity with frequency at different temperatures.

Fig.7d shows the frequency dependence of DC conductivity (σ_{dc}), it can be seen that, for all ULN crystal the DC conductivity increases with the increase of temperature. The defect concentration of the crystal increases exponentially with increase of temperature, consequently the electrical conduction of the crystal also increases. In the present study, it is concluded that the conduction region of the crystal is considered to be connected with the mobility of the vacancies.

CONCLUSION

Optical quality crystals of semi-organic Urea Lead nitrate (ULN) with the molecular formula ($CN_2H_4O.Pb(NO_3)_2$) have been successfully grown by slow evaporation method. The grown crystals were characterized using single crystal X-ray diffraction analysis, which shows that the ULN crystals are belongs to hexagonal system. The presence of functional groups of ULN and the bond interaction on between urea and lead nitrate have been confirmed by FTIR analysis. Optical studies show that the ULN crystals have a wide transparency window in the entire visible region, making it an ideal candidate for NLO device applications. The TG-DTA studies reveal that the crystal is thermally stable up to ~527.4°C and the mechanism responsible for the weight losses is discussed. The low value of dielectric loss (ε_r) at high frequencies suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications

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