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Synthesis, growth and characterisation of nonlinear optical material L-proline zinc chloride single crystal

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ABSTRACT

Single crystals of semiorganic nonlinear optical material L-proline zinc chloride (LPZC) were synthesized and grown by slow evaporation technique. The lattice parameters and space group were determined using single crystal XRD analysis. The optical transmittance and the lower cut-off wavelength of the LPZC was identified by UV–VIS–NIR studies. The modes of vibrations of different molecular groups present in the sample were identified by the FTIR spectral analysis. Dielectric measurement of LPZC was also carried out. The activation energy has been calculated using Arrhenius plot of ac conductivity.

INTRODUCTION

Nonlinear optics is one of the most attractive fields of current research in view of the applications in the areas such as optical modulation, optical switching, optical logic, frequency shifting and optical data storage and for developing technologies in telecommunication and signal processing [1,2]. Investigations were initially focused on purely inorganic materials, which were the first to demonstrate second-order nonlinear optical properties [3]. Attention was later directed towards organic materials due to their low cost, fast and large nonlinear response over a broad frequency range and inherent synthetic flexibility of high optical damage threshold [4]. However, organic materials are poor in thermal stability and mechanical hardness. It is difficult to grow large size and high quality single crystals. Recently, several complexes of proline were reported such as L-proline cadmium chloride monohydrate and L-proline lithium chloride monohydrate [5]. In the present study, L-proline zinc chloride (LPZC) was grown by slow solvent evaporation technique. The grown crystal was subjected to single crystal XRD study to understand the crystal system and space group. The transparency range of the crystal was estimated from UV-VIS-NIR spectrum to find out whether the material can transmit the laser beam in the wavelength range of 200 – 1600 nm for frequency conversion. The dielectric property of the material was not properly studied so far with respect to NLO behaviour.

2. Synthesis and Growth of LPZC crystal

L-proline zinc chloride was synthesised by taking L-proline and zinc chloride in 2:1 stoichiometric ratio. The required amount of starting materials for the synthesis of LPZC was calculated according to the reaction.

$$ZnCl_2 + NH_2CH_2CH_2CH_2CHCOOH \rightarrow Zn\,(NH_2CH_2CH_2CH_2CHCOOH)\,Cl_2$$

The calculated amount of L-proline was first dissolved in deionized water. Zinc chloride was then added to the L-proline solution by stirring for 24 hours. The prepared solution was allowed to evaporate at room temperature. After a period of 25 days, single crystal of LPZC with dimensions of 11×4×4 mm^3 were harvested successfully. The photograph of as-grown LPZC single crystal is shown in Fig. 1.

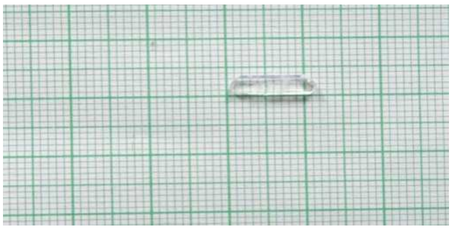

Fig.1 Photograph of the as-grown LPZC single crystal.

RESULTS AND DISCUSSION

3.1. Single crystal X-ray diffraction

Single crystal XRD study reveals that the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$. The lattice parameters are found to be a= 6.6155 Å, b=13.5574 Å, c= 16.2532 Å, $\alpha=90^0$, $\beta=90^0$, $\gamma=90^0$ and volume= 1457.7 $(Å)^3$. The space group suggests that the grown crystal is noncentrosymmetric. The data obtained are found to be in good agreement with the reported values [6].

3.2. UV-VIS-NIR spectrum

UV-VIS-NIR spectrum was recorded using CARY 5E UV-VIS-NIR SPECTROPHOTOMETER in the wavelength range of 200 – 1600 nm and shown in Fig. 2. From the spectrum, the UV cut-off wavelength is found to be 233 nm which is in good agreement with the reported value [7]. The crystal possesses the second harmonic generation.

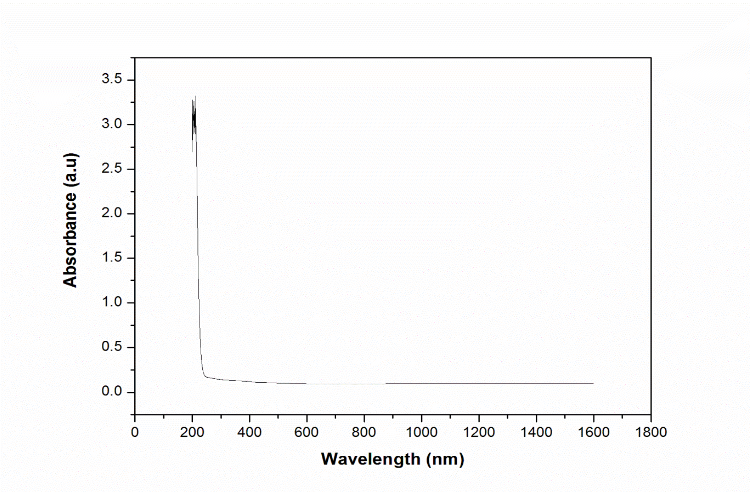

Fig. 2 UV-VIS-NIR spectrum of LPZC single crystal.

3.3. Dielectric Studies

The dielectric constant and loss were measured in the frequency range from 50 Hz to 5MHz at various temperatures for the grown LPZC crystal. Good quality crystal was selected for dielectric studies. The dielectric constant was calculated using the relation

$$\varepsilon' = \frac{Cd}{A\varepsilon_0} \qquad (1)$$

where C is the capacitance , d is the thickness and A is the area of the sample. The plot of dielectric constant versus frequency is shown in Fig.3 at the temperatures 313 K, 323K,333 K and 343 K. It is observed that the dielectric constant decreases with increase in frequency. The large values of dielectric constant at low frequency enumerate that there is a contribution from all four known sources of polarization, namely electronics, ionic, dipolar and space-charge polarizations. Space charge polarization is generally active at lower frequencies and high temperatures. Further the space charge polarization is dependent on the purity and perfection of the material. The characteristics of low dielectric constant at high frequency suggest that the sample possesses enhanced optical quality with fewer defects.

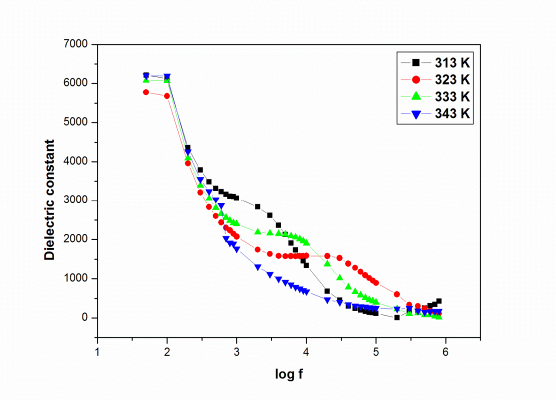

Fig.3. Variation of dielectric constant of LPZC crystal as a function of frequency at different temperatures.

3.4. A.C. conductivity studies

The a.c conductivity of LPZC was evaluated using the relation

$$\sigma_{ac}=2\pi f\varepsilon_o\varepsilon_r\tan\delta \qquad (2)$$

where ε_o is the vacuum dielectric constant, ε_r is the dielectric constant, f is the frequency of ac applied and tanδ is the dielectric loss. Fig.4 shows the variation of ac conductivity with frequency. The ac conductivity is zero up to 1 MHz and starts increasing from 1 MHz onwards. This is due to the fact that the relaxation times of charge carriers are not matching with the time period of the applied ac field up to 1 MHz and so the conductivity of the material is almost zero. The variation of ac conductivity with temperature follows the Arrhenius plot of equation as,

$$\sigma_{ac}=\sigma_o\exp(-E_a/kT) \qquad (3)$$

where E_a is the activation energy, k is the Boltzmann constant and T is the temperature (in Kelvin). Fig.5 shows the plot of $\ln\sigma_{ac}$ versus temperature. As the temperature is increased, the ac conductivity is found to increase. When the temperature is increased, the thermal energy sufficiently increases to enhance the movement of charge carriers for increasing the ac conductivity. The activation energy value is found to be 0.021913 eV and the lower value of activation energy establishes that the crystal contains less number of defects. Defect free crystals are generally more useful for device fabrications.

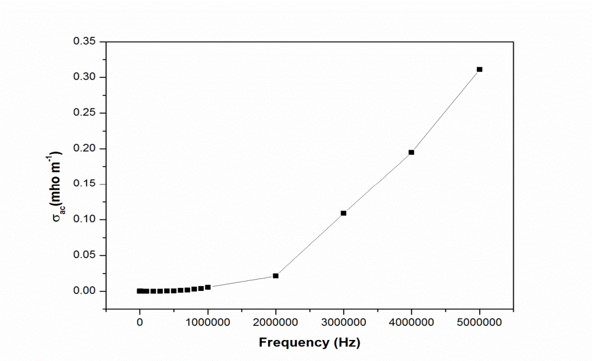

Fig.5. Plot of ac conductivity of LPZC versus frequency

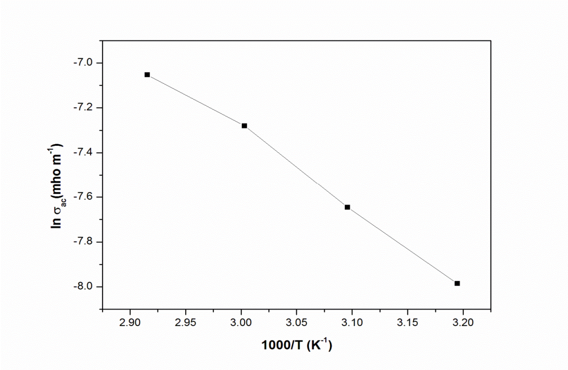

Fig.6. Plot of ac conductivity of L-PZC versus temperature

CONCLUSION

Good quality crystals of LPZC were grown by slow evaporation technique. It is found that the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$. The space group of the grown crystal reveals that the crystal is non-centrosymmetric. The transparent nature of the material was confirmed from the studies of UV-VIS-NIR spectrum. The ac conductivity was analysed from the dielectric studies.

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