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A strategic approach to physico-chemical analysis of bis (thiourea) lead chloride – A reliable semi-organic nonlinear optical crystal

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ABSTRACT

Good quality crystals of bis thiourea lead chloride (BTLC) have been grown by slow evaporation method from aqueous solution. Orthorhombic structure and $Pna2_1$ space group of the crystals have been identified by single crystal X-ray diffraction. Studies on nucleation kinetics of grown BTLC has been carried out from which meta-stable zone width, induction period, free energy change, critical radius, critical number and growth rate have been calculated. The experimental values of interfacial surface energy for the crystal growth process have been compared with theoretical models. Ultra violet transmittance studies resulted in a high transmittance and wide band gap energy suggested the required optical transparency of the crystal. The second harmonic generation (SHG) and phase matching nature of the crystal have been justified by Kurtz-Perry method. The SHG nature of the crystal has been further attested by the higher values of theoretical hyper polarizability. The dielectric nature of the crystals at different temperatures with varying frequencies has been thoroughly studied. The activation energy values of the electrical process have been calculated from ac conductivity study. Solid state parameters including valence electron plasma energy, Penn gap, Fermi energy and polarisability have been unveiled by theoretical approach and correlated with the crystal's SHG efficiency. The values of hardness number, elastic stiffness constant, Meyer's Index, minimum level of indentation load, load dependent constant, fracture toughness, brittleness index and corrected hardness obtained from Vicker's hardness test clearly showed that the BTLC crystal has good mechanical stability required for NLO device fabrication.

1. Introduction

Non linear optical (NLO) materials are of vital importance for various applications in the domain of frequency conversion, photonics and optoelectronic technology [1]. In the current scenario, material scientists are showing a keen interest on NLO semi-organic complexes owing to their ability to combine the flexibility of organic materials with the mechanical strength and thermal stability of inorganic materials [2]. Synthesis of semi-organic NLO crystals and their subsequent characterization towards device fabrication have attained great impetus in view of their significance in academics and industrial applications. One such semi-organic material class is the metal complex of thiourea. Thiourea molecule, due to its large dipole moment, is capable of forming an extensive network of hydrogen bonds. Although thiourea is a centrosymmetric molecule it becomes non-centrosymmetric on metal coordination which is an essential property for a crystal to exhibit nonlinear optical activity [3]. The well known thiourea complexes reported in the literature include bis (thiourea) cadmium chloride [4], bis (thiourea) zinc chloride [5], and bis (thiourea) strontium chloride [6]. Along this direction we have chosen bis (thiourea) lead chloride (BTLC), for which only crystal structure [7] and a few basic studies have been reported [8].

A thorough knowledge of kinetics parameters are of great value in growing high quality crystals. In the present investigation, crystal growth kinetics parameters of BTLC crystals, including meta-stable zone width, induction period, interfacial energy, critical number, free energy change, critical nucleus radii and nucleation rate have been elucidated. To ensure the required optical quality and electronic structure of single crystal, the UV–visible spectral studies have been performed. The SHG efficiency and phase matching nature of BTLC crystals have been revealed by Kurtz-Perry method. The frequency dependence of dielectric properties gives a clear insight into the material applications. In this regard, the dielectric studies with variable temperature and frequencies have been performed from which various solid state parameters have been deduced. As micro hardness shares a direct correlation with the crystal structure and is sensitive to inter

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atomic spacing and lattice perfection [9], the Vickers hardness studies have been extensively done to arrive at the values of important mechanical parameters of BTLC crystals.

2. Experimental procedure

2.1. Synthesis and solubility test of BTLC

In the present study, bis (thiourea) lead chloride (BTLC) crystals have been grown by slow evaporation method. Commercially available (AR grade E-Merck) lead chloride and thiourea have been taken in 1:2 ratio and dissolved in deionised water. The resultant solution has been stirred thoroughly by a magnetic stirrer. As thiourea has strong coordinating capacity to form different phases of metal-thiourea complexes, the thorough stirring is needed to avoid co-precipitation of multiple phases. The synthesis has been carried out as per the following chemical reaction.

$$PbCl_2 + 2\,CS[NH_2]_2 \rightarrow Pb[CS(NH_2)_2]_2Cl_2$$

In the view of choosing the proper solvent and optimum temperature to grow high quality crystals, a solubility test has been adopted. The solubility test has been performed using the synthesized BTLC solute and water solvent. The solution was stirred well using a motorized magnetic stirrer and placed in a constant temperature bath maintained at 303 K. When the super-saturation is attained, the equilibrium concentration of the solute has been analyzed using gravimetric technique [10]. The technique has been repeated for temperatures 308, 313, 318 and 323 K.

2.2. Meta-stable zone width and induction period measurements

The saturated solution of BTLC has been prepared according to the solubility data. For performing nucleation studies, a constant volume of 100 ml of saturated solution has been taken in a constant temperature bath for five different temperatures (303, 308, 313, 318 and 323 K). As per the poly-thermal method [11], the saturated solution has been carefully cooled from the preheated temperature to the nucleation temperature where the first visible critical nucleus has been observed. The meta-stable zone width has been determined as the difference between nucleation temperature and saturation temperature. In practice, wider meta-stable width is preferred for growing good quality crystals. The solubility and nucleation curves are shown in Fig. 1a. The solubility curve shows a positive solubility gradient. The study of induction period helps to modify and control the nucleation rate for preparing good quality crystals. As per isothermal method [12], the induction period is the time taken for forming the critical nuclei at a particular temperature. The correctness of the observed induction period values has been ascertained by repeating the experiments.

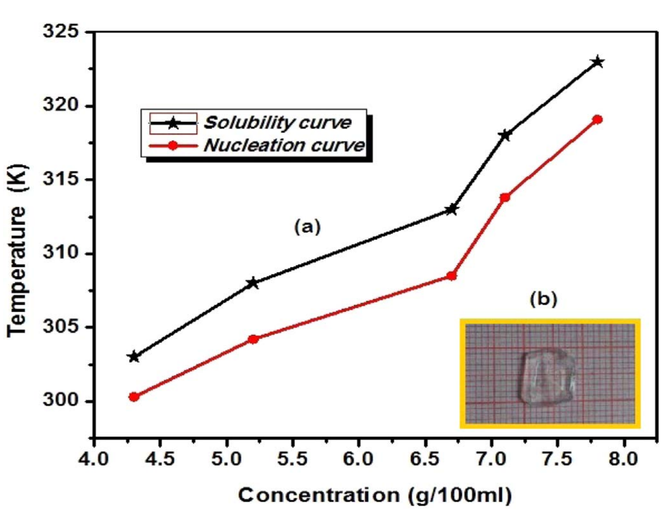

Fig. 1. (a) Meta-stable zone width of bis thiourea lead chloride (b) photograph of bis thiourea lead chloride crystal.

2.3. Crystal growth

Single crystals of BTLC have been grown from the saturated aqueous solution by slow evaporation method. The solution has been thoroughly filtered by using Whatman filter paper into a glass beaker, covered well with a perforated polythene cover for restricting the fast evaporation and kept undisturbed in a dust free atmosphere. After a span of 28 days, good quality BTLC crystals have been harvested. The photograph of the grown crystal of BTLC is shown in Fig. 1b.

2.4. Analytical techniques

The grown crystals have been characterized by single crystal X-ray diffraction studies using Enraf (Bruker) Nonius CAD4 diffractometer with Mo Kα (λ=0.7170 Å). The optical transmission spectra of BTLC crystals have been recorded in the region of 200–800 nm using Shimadzu UV-106 spectrometer. The SHG and phase matching efficiency of the grown crystals have been measured by Kurtz second harmonic generation (SHG) test using a Quanta ray spectra physics Nd:YAG laser. The dielectric studies on the BTLC crystals have been carried out by the parallel plate capacitor method as a function of temperatures for various frequencies (range of 50 Hz–5 MHz) using Hiocki model 3532-50 LCR Hitester instrument. The mechanical hardness studies have been performed using Leitz–Wetzlar hardness tester fitted with a diamond indenter.

3. Results and discussion

3.1. X-ray diffraction studies

Single crystal X-ray diffraction analysis of BTLC crystal suggests that the BTLC crystal crystallizes in orthorhombic structure with non-centrosymmetric space group $Pna2_1$. The obtained axial cell lengths dimensions are a=21.28 Å, b =4.14 Å, c=11.90 Å, Volume V=1048.38 $(Å)^3$, the inter facial angles α=β=γ=90°. The experimental values were in accordance with the reported values [7].

3.2. Nucleation kinetics

3.2.1. Theoretical approach

The interfacial surface energy prevailing between the crystal and its surrounding saturated solution significantly influences the crystal growth and the nucleation rate [13]. Nielson and Sohnel [14] arrived at a relation to find out the interfacial surface energy (γ) which states

$$\gamma = (kT/hd^2) \times \ln(C/C_0) \quad (1)$$

where, k is Boltzmann constant, d is the mean diameter of ions, h is the hydration number which varies from 3.4 to 5, C and C_0 are the mole fractions of solute in the super saturated and saturated solution respectively at temperature T. Another expression to calculate interfacial surface energy was put forward by Sangwal [15] as

$$\gamma = [kT] \times [\{3 - \ln(C/C_0)\}/8\,d^2] \quad (2)$$

Christoffersen et al. [16] deduced an expression for interfacial surface energy based on the theory of surface nucleation as

$$\gamma = 0.282 \times (k\,T/d^2) \times \ln(C/C_0) \quad (3)$$

Using the Eqs. (1–3) the values of interfacial surface energy have been computed and presented in Table 1.

3.2.2. Experimental approach

As per the classical theory of homogeneous spherical nucleus