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Synthesis, structural, topographical, linear and nonlinear optical, electrical and mechanical properties of Bisthiourea zinc acetate single crystal

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ABSTRACT

Nonlinear optical material Bisthiourea Zinc Acetate (BTZA) was synthesized by slow evaporation solution growth technique. The grown crystals were characterised by Single crystal XRD and powder XRD studies. The presence of functional groups and the co-ordination of metal ions to Thiourea were confirmed by FTIR analysis. The UV-vis −NIR spectrum shows a low absorption in the entire visible and IR region. Optical band gap of the grown crystal was found to be 4.18 eV. The photoluminescence studies carried out and the crystal has blue emission. The Refractive Index was determined experimentally for the first time and found to be 1.508 for the incident wavelength of 632.8 nm. The second harmonic generation efficiency was determined using Kurtz and Perry powder technique and it was 0.7 times than that of the KDP crystal. Thermal properties were studied by thermo gravimetric analysis and differential thermal analysis. Dielectric studies were carried out at different frequencies for various temperatures. The mechanical behaviour of the grown crystal was studied using Vickers micro hardness tester. The growth mechanism and surface features are investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

1. Introduction

Non Linear Optical (NLO) materials are attracting a great deal of attention due to their applications in optical devices, such as optical switches, optical modulators, optical communications, optical data storage and etc [1,2]. In the past few decades, organic and semi-organic materials are the most widely used crystals for frequency conversion. Organic crystals have a large nonlinear coefficient but are very sensitive to the presence of intrinsic defects and phonon subsystem [3,4]. Inorganic crystals have high thermal and mechanical stability than that of organic crystals [5,6]. Recent interest lies in semi-organic materials as it combines the positive aspects of organic and inorganic materials without intrinsic defects.

Semiorganic materials possess large nonlinearity, high resistance to large induced damage, low angular sensitivity and good mechanical hardness [7–9]. Semi-organic complexes of thiourea are interesting because of their large nonlinear property, lower UV cut off, wide transparency and good thermal stability [10]. Thiourea is an interesting inorganic matrix modifier due to its large dipole moment and has the ability to form extensive network hydrogen bonds [11]. Thiourea is centrosymmetric which yields excellent non-centrosymmetric materials when it is incorporated into the respective inorganic salt [12]. Some of the potential Thiourea complexes are Zinc Thiourea chloride (ZTC) [13], Zinc Thiourea Sulphate (ZnTS) [14], Bisthiourea Cadmium Chloride (BTCC) [15], Bisthiourea Cadmium Acetate (BTCA) [16]. Growth and various characterization of Bisthiourea Zinc Acetate has already been reported [12,17–21]. In this paper, XRD, topographical, linear and nonlinear optical, electrical and mechanical properties of Bisthiourea Zinc Acetate (BTZA) are reported. Refractive index, AFM analysis Photoluminescence are measured for the first time and reported.

2. Experimental procedure

2.1. Synthesis and crystal growth

The Bisthiourea Zinc acetate was synthesized by mixing Zinc Acetate and Thiourea (AR grade) in the ratio of 1:2 in deionised

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water at room temperature. Purity of the synthesized salt was improved by successive recrystallization process. Care was taken during heating of the solution and the temperature was maintained as low as 45 °C in order to avoid any decomposition. Optically good quality single crystals were harvested in a span of 20 days which are transparent and non-hygroscopic. The as grown crystals are shown in Fig. 1.

2.2. Solubility

The solubility of the BTZA crystal was determined by dissolving the crystals in deionized water taken in an air tight container, maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute is analyzed gravimetrically. The same procedure was followed to determine the solubility in ethanol. The temperature dependence curve of solubility for both the solvents is shown in Fig. 2. From the graph, it is found that the solubility increases with the temperature and possesses positive temperature gradient of solubility for both the solvents with good solubility in water.

3. Results and discussion

3.1. Single crystal and powder X-Ray diffraction analysis

The space group and cell parameters were determined by the single crystal diffraction on a BRUKER axs SMART APEXII. From the XRD analysis, it is observed that the BTZA crystal belongs to monoclinic structure with space group of $P2_1$. The cell parameter values obtained are a = 7.090 Å, b = 17.664 Å, c = 11.167 Å and volume = 1361 $Å^3$ which are well agreed with the reported values [22].

The morphology of the as grown crystal was also done using Enraf Nonius CAD4-MV31 diffractometer as shown in Fig. 3. It was observed that the length of the crystal is along the 'a'axis, which resulted in elongation along [100] direction. The 'b' and 'c' axes does not show any developed planes. The prominent planes are $(01\bar{1})$, $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, $(1\bar{1}0)$, (110), $(0\bar{1}\bar{1})$, $(0\bar{1}1)$ and (011). The planes (011) and $(0\bar{1}\bar{1})$ are the most prominent plane and the other well-developed planes are $(01\bar{1})$ and $(0\bar{1}1)$ that dominates the crystal morphology. The morphology studies indicate that the BTZA crystal grows faster along the [100] direction. The crystallographic unit cell has the shortest dimension along 'a' direction. Hence it is inferred that fastest growth of crystal occurs along the shortest crystallographic axis.

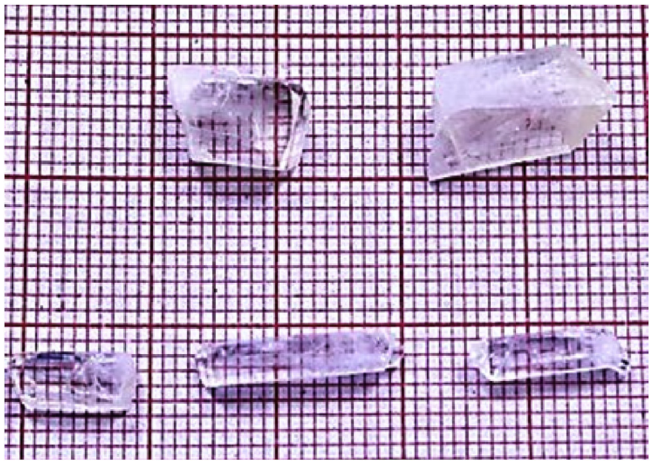

Fig. 1. As grown crystals of BTZA.

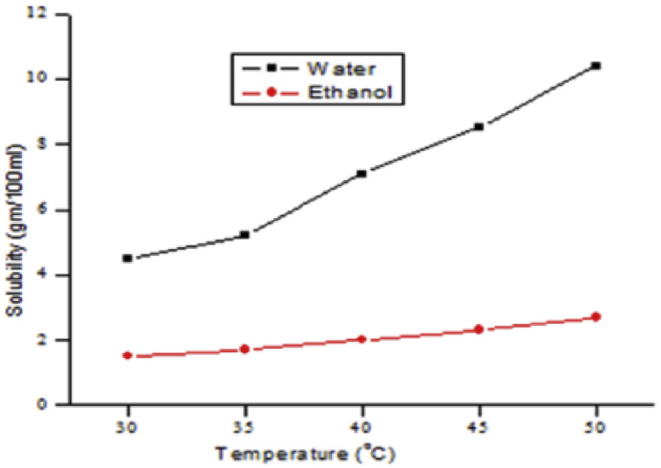

Fig. 2. Solubility curve of BTZA.

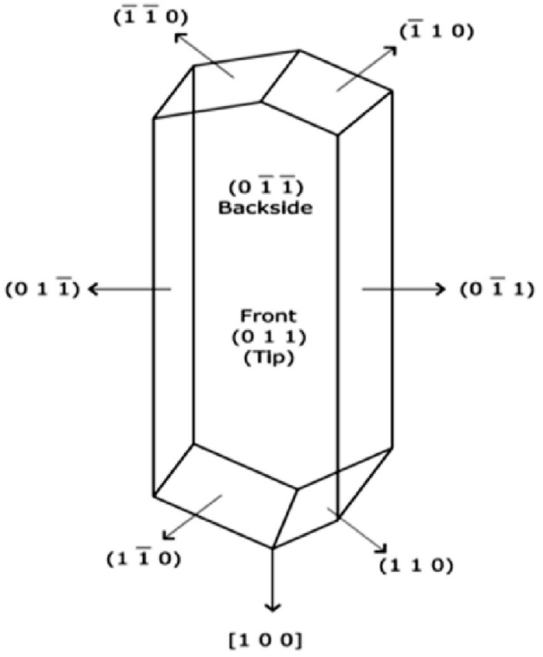

Fig. 3. Morphology of BTZA.

Powder X-ray Diffraction pattern was recorded using CuKα (K = 1.5418 Å) radiation by crushing the BTZA crystal into fine powder. The diffraction pattern was scanned over the range of 10–70 °C at a scanning rate of 1°/minute. The intensity of the diffracted beam was recorded as a function of 2θ and the peaks were indexed as shown in Fig. 4 that confirms the perfection of good quality single crystal.

3.2. FTIR spectroscopic analysis

The FTIR spectra of the grown crystal were recorded in the KBr phase in the frequency range of 450–4000 cm^{-1} using a Perkin Elmer Spectrum1 FTIR spectrometer as shown in Fig. 5. In BTZA, the zinc can coordinate either with the nitrogen or sulphur in thiourea molecule. The extensive hydrogen bonding in the complex is proved from the broadening of the spectrum in the range of