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Bulk crystal growth and characterization of non-linear optical bisthiourea zinc chloride single crystal by unidirectional growth method

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A B S T R A C T

The unidirectional crystal growth method has been employed for the bulk growth of semi-organic non-linear optical bisthiourea zinc chloride single crystal along *a*-axis with high solute-crystal conversion efficiency. Single crystal X-ray diffraction studies confirm the orthorhombic structure. Optical studies reveal very high transmission of the crystal along the growth axis. Dielectric study shows that the dielectric constant decreases with increase in frequency. Microhardness measurements along the growth axis enunciate the favorable hardness behavior.

1. Introduction

Non-linear optical (NLO) materials have attracted and gaining enormous demand due to their wide applications in the recent technologies like lasers, optoelectronics, optical communication and data storage systems [1,2]. Semi-organic crystals have been proposed as a new approach for molecular engineering with interesting optoelectronics and non-linear optical properties [3,4]. The excellent optical quality is one of the criteria for non-linear optical crystals for constructive applications. Recently, few researchers have used uniaxial solution crystallization technique for the growth of NLO crystals for laser applications, which is confined to grow the crystals along an application oriented plane [5–8]. Also, the main advantage of unidirectional solution growth technique is simple experimental setup, high solute-solid conversion efficiency and minimum thermal stresses on the crystal during growth and prevention of the microbial growth. The achievement of high solute-crystal conversion efficiency reduces the preparation and maintenance of growth solution to a large extent because in conventional solution growth method, in order to grow such a large sized crystal, a large quantity of solution in a large container is normally used and only a small fraction of the solute is converted into a bulk single crystal. But, in the present method, the entire quantity of the solute is converted into crystal thus achieving solute-crystal conversion efficiency of hundred percent [9]. Bisthiourea zinc chloride (BTZC) is a semi-organic high non-linear optical crystal having excellent figure of merit [10,11]. In the present work, the bulk single crystal of BTZC has been grown by uniaxial method with a slight modification in the growth apparatus. The grown crystals were subjected to single crystal X-ray diffraction (XRD) analysis, UV–vis–NIR spectral analysis, dielectric studies and Vickers hardness test.

2. Experimental

2.1. Synthesis and crystal growth

Bisthiourea zinc chloride (BTZC) was synthesized by mixing aqueous solution of zinc chloride and thiourea (99%) in the ratio of 1:2 and the chemical reaction is given as:

$$ZnCl_2 + 2CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]_2Cl_2, \quad (1)$$

The product was purified by repeated re-crystallization before it is used for crystal growth runs.

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2.2. Solubility studies and seed selection

The solubility of the synthesized salt was carried out using deionized water at various temperatures ranging from 303 to 328 K in 5 K intervals by gravimetric analysis [12]. The solubility curve of BTZC is shown in Fig. 1. From the plot, it was observed that the sample shows positive solubility; with 24 g/100 ml at 312 K. The supersaturated solution was prepared in accordance with the solubility data and allowed for slow evaporation at 312 K. From the morphology pattern (Fig. 2) of BTZC, the (0 1 1) plane was observed to be quite favorable for the growth experiments. The selected seed in the (0 1 1) plane was polished further using deionized water and mounted at the bottom of the ampoule.

2.3. Growth setup and crystal growth

The growth setup used here is a modified version of the SR method and our earlier reported one [13] and is shown in Fig. 3. It consists of a heating coil, thermometer, inner container, temperature controller, growth vessel and water bath. A ring heater fixed at the top of cylindrical glass tube of diameter 10 cm and height 40 cm was used as inner container and a short cylindrical constant temperature water bath as outer container. The assembly was designed in such a way to obtain a maximum temperature profile at the top. The ring heater connected to microprocessor-controlled

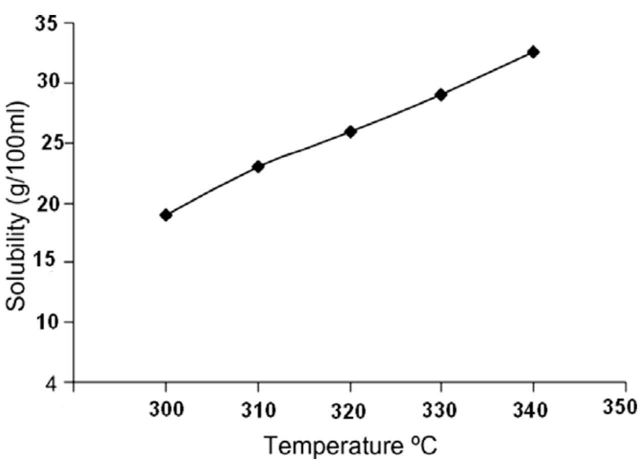

Fig. 1. Solubility curve of BTZC.

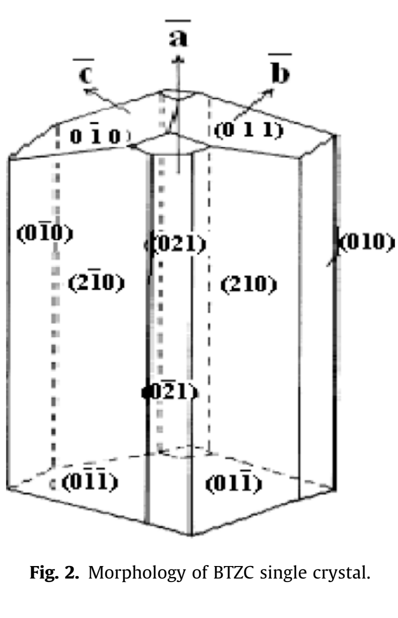

Fig. 2. Morphology of BTZC single crystal.

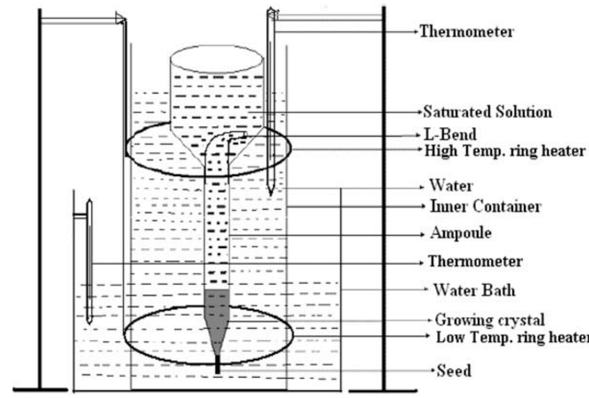

Fig. 3. Crystal growth setup.

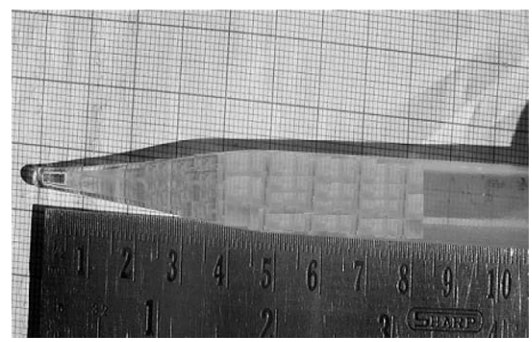

Fig. 4. Photograph of SR grown BTZC single crystal.

thermocouple provides a constant temperature 318 K at the top of ampoule. A seed was fixed at the bottom of the ampoule and filled with the saturated solution of BTZC, which was mounted along the axis of the inner cylinder. The ampoule was designed with an inner L-bend, which controls spontaneous nucleation on the top wall of the ampoule and prevents poly crystallization. The water level inside the water bath was increased with respect to the growth in the ampoule. The temperature gradient creates a concentration gradient along the growth ampoule, having a maximum super saturation at the bottom of the ampoule and a minimum at the top of the ampoule, there by avoiding any possibility of a spurious nucleation along the length of the ampoule. The excess solute generated by evaporation of the solution is driven down the ampoule by the temperature gradient of the setup. Thus, the growth was initiated from the seed fixed at the bottom of the ampoule with desired orientation along it's *a*-axis. The growth rate of the crystal was found to be 5 mm per day. The crystals of 80 mm length and 10 mm diameter have been grown successfully with in a period of 16 days. The grown crystal shows a cylindrical morphology and the photograph of the grown crystal is shown in Fig. 4.

3. Results and discussion

3.1. Single crystal X-ray diffraction

The grown crystals were subjected to single crystal X-ray diffraction using ENRAF NONIUS CAD-4 single-crystal X-ray diffractometer with Mo Kα radiation (λ = 0.7170 Å) to determine the unit cell dimensions. A good quality crystal of dimensions $4 \times 2 \times 2$ mm^3 was selected for the X-ray diffraction studies. The grown crystal is found to be crystallized in the orthorhombic system with space group $Pn2_1a$, crystallographic data are reported