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Growth, optical and thermal characterization of bis(thiourea)zinc chloride single crystals

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Abstract

Single crystals of nonlinear optical material bis(thiourea)zinc chloride (BTZC) were successfully grown by the temperature lowering method and also by the slow evaporation method at constant temperature 28.5 °C from its aqueous solutions having various pH values. The best quality crystal was obtained at pH value of 3.13. Studies on structural, thermal properties of the crystals have been carried out on the basis of X-ray diffraction (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA) and thermogravemetric analysis (TGA). DTA study indicates the possibility of structural changes without weight loss. The values of specific heat calculated from DSC data indirectly demonstrate the high damage threshold of BTZC crystal. The crystals possess wide optical transmission window between 290 nm and 2000 nm. Kurtz powder SHG measurement confirms the nonlinear optical property of the grown crystals.

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1. Introduction

For several years, an intense search for new NLO materials has been carried out by many workers and a wide variety of both organic and inorganic NLO materials has been developed. Problems with both classes of materials have resulted in the investigation of semiorganics [1–6]. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. Hence recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [7,8]. In search of these semiorganic NLO materials urea and urea analogs have been explored [9]. Among these, bis(thiourea)zinc chloride (BTZC) is a potential semiorganic nonlinear optical material and crystallizes in the noncentrosymmetric orthorhombic space group $Pn2_1a$ [10]. The unit cell dimensions of BTZC are $a = 13.065$ Å, $b = 12.722$ Å, $c = 5.890$ Å and $V = 978.99$ Å^3. Growth of bulk single crystal of BTZC by slow evaporation technique at room temperature has been reported by Dhanuskodi et al. [11]. In our present study we have attempted to grow optically clear crystal of BTZC by optimizing the pH value of the growth solution at 3.13 by both slow evaporation and slow cooling method. The structural, thermal and optical characterization of the grown crystals were then made by XRD, FTIR, DTA, TGA, DSC, optical transmission and second harmonic efficiency measurements. We have also calculated the specific heat of BTZC from the DSC data. Finally the quality of grown crystal is checked by chemical etch pit study.

2. Synthesis and crystal growth

The BTZC crystals were synthesized from $ZnCl_2$ and thiourea solution followed by the given reaction:

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$ZnCl_2 + 2[CS(NH_2)_2] = Zn[CS(NH_2)_2]_2Cl_2$

In order to achieve this, required amount of $ZnCl_2$ salt and thiourea were dissolved separately in water with continuous stirring using a magnetic stirrer and heating at a constant temperature of 55 °C until a clear homogeneous solution was formed. The two homogeneous solutions were then mixed together and heated at the same temperature with vigorous stirring. This process was continued for 6–7 h and the final solution was kept in a glass vessel with perforated lid for crystallization. In this way several solutions of BTZC were made at different pH values. After 2–3 weeks BTZC crystals of different sizes and quality were obtained. These crystals of good quality were used as the seed crystals for slow cooling technique. For slow cooling technique a saturated solution of BTZC was prepared at 55 °C. The seed crystal was then hanged in this clear saturated solution of BTZC. The temperature of the solution was dropped at a rate of 0.5 °C/day until a temperature of 35 °C was reached. For this purpose we have used a microprocessor controlled crystallization bath. The overall process took 40 days and crystals of appreciable size were obtained.

3. Characterization studies

3.1. X-ray diffraction analysis

In order to confirm crystallinity of the grown crystals and also the unit cell parameters, the X-ray diffraction analysis was carried out using the powder sample of BTZC. The X-ray intensity data of the powder sample of BTZC was recorded on a microprocessor controlled X-ray diffractometer (SEIFERT XRD 3000P) using nickel filtered CuK_α radiation (36 KV, 20 mA). The sample was scanned in steps of 0.02° (for a time interval of 2 s over a 2θ range from 8° to 50°.

3.2. FTIR studies

The functional groups present in the grown crystals were analyzed using FTIR spectrum. The FTIR spectra of BTZC were obtained from potassium pellets on a Nicolet MAGNAIR 750 (series II) FTIR spectrometer.

3.3. Thermal studies

As far as the fabrication technology is concerned, the study of thermal behavior of BTZC is of immense importance. For this study we have performed the DTA, TGA and DSC analysis. The DTA and TGA analysis were carried out simultaneously with the help of an instrument (SDT Q600 V8.2) using BTZC as the sample and alumina as reference. The powder sample of BTZC was heated at a rate of 10 °C/min in protected nitrogen gas flow.

For DSC analysis we have heated the sample at a lower rate of 5 °C/min using a Perkin–Elmer differential scanning calorimeter in the temperature range 40–140 °C.

3.4. Optical studies

3.4.1. Optical transmission

Optical transparency of BTZC crystal was measured by a Hitachi U-3500 spectrophotometer in the wavelength range 200–2000 nm. The light path direction was normal to (010) and the thickness of the sample was 2.0 mm.

3.4.2. Second harmonic generation (SHG) efficiency

The second harmonic generation efficiency of BTZC was determined by powder technique of Kurtz and Perry [12]. The second harmonic output was generated by irradiating the powder samples by a pulsed laser beam. The source is a Nd-YAG laser with a pulse width of 8 ns and pulse energy of 5 mJ. The output from the sample was filtered by an IR filter to eliminate the fundamental beam and the second harmonic wave was focussed by a lens and measured by a photomultiplier tube.

3.5. Quality study

For fabrication of devices we need good quality crystals of our interests. The quality of the grown crystals are usually assessed by knowing the defect contents of the crystals. There are several ways to find out the defect structure of the crystals. In our case we have implemented the chemical etch pit method to assess the defect contents or quality of the crystals. For this study some organic solvents like water, ethanol etc were selected as etchants. Transparent crystals free from inclusion were chosen for etch pit study. The crystals were dipped in the etchants for a few seconds to few minutes and the etch patterns were observed under an optical microscope. The number of etch pits per unit area were then counted to reveal the dislocation density of the grown crystals.

4. Results and discussion

It has already been mentioned in the crystal growth section that BTZC crystals were grown from its aqueous solution of different pH values. The grown crystals harvested after 2–3 weeks show different morphologies and qualities. At pH values higher than 5.0 the grown crystals are needle in shape where the needle axis is in [100] direction. At a lower pH values the growth rate along other two directions [010] and [001] increases resulting into a crystal of rectangular dimensions. The best quality crystals were obtained by slow *evaporation* technique at a pH value of 3.13 *as* shown in Fig. 1. Now to confirm the lattice parameters of the grown crystals, reflection lines of the X-ray powder diffraction pattern (Fig. 2) were indexed and the unit cell parameters were calculated using the computer program