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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.4, pp 1671-1677, 2015

Growth and characterization analysis of BTZC single crystals grown by SR and conventional method

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Abstract: Single crystals of Bisthiourea zinc chloride (BTZC) were successfully grown by Sankaranarayanan-Ramasamy(SR) method and conventional methods. Single crystal X-ray diffraction study reveals that BTZC crystallizes into orthorhombic system with the space group $Pn2_1a$. The unidirectional growth of BTZC along the plane (0 1 1) was confirmed from the powder XRD pattern with the sharp peak having maximum intensity. The UV-Visible spectral study reveals improved transparency for the SR grown crystal. Vickers hardness test brings forth higher hardness value for the SR grown BTZC as compared to conventional grown BTZC crystal. The dielectric measurement exhibits very low dielectric constant and dielectric loss at higher frequencies for both the conventional and SR method BTZC. A comparative damage threshold analysis made on the BTZC crystals by conventional and unidirectional method shows that the crystal grown by SR method has higher damage threshold.
Keywords: Growth from solutions, Optical properties, Optical constant, Mechanical Properties.

1. Introduction

Nonlinear optical materials are capable of producing higher values of the original frequency and find applications in optical modulation, fiber optic communication and opto-electronics [1,2]. In recent years, many researchers have tried to find varieties of NLO crystals for laser applications [3–6]. Inorganic crystals are widely used in these applications because of their high melting point, high mechanical stability and high degree of chemical inertness [7]. The optical nonlinearity of inorganic crystals is generally lower than that of the optical device demand. Organic compounds are often formed by weak vander Wall's, hydrogen bonds and possess a high degree of delocalization [3–6]. A major drawback of organic NLO crystals is the difficulty in growing large size, good optical quality and higher mechanical stability single crystals. NLO properties of semi-organic materials are currently under intense investigation, triggered by potential applications in NLO due to their incorporated advantages of both organic and inorganic crystals [8]. Among the various classes of semi-organic nonlinear optical materials, metal complexes of thiourea have received potential interest, because they can be effectively used as the better alternatives for KDP crystals in frequency doubling process and laser fusion experiments [9, 10]. As thiourea molecules possess a large value of dipole moment, they can form number of metal coordination compound like zinc thiourea chloride (ZTC), bis-thiourea cadmium chloride (BTCC), zinc (tris) thiourea sulfate (ZTS), tris-thiourea copper chloride (TCC) etc., [11-13]. In this series, a NLO single crystal of Bisthiourea zinc chloride (BTZC) is found to be a good candidate for NLO applications.[14]

Growth, and characterization of conventional slow evaporation method grown BTZC single crystal have been reported [15]. However the conventional grown crystals have a small size, different morphology, with many faces and poor transparency. For devices we need a large size, defect-free, mechanically and optically good quality single crystals. The crystal with specific orientation can be grown from solution by Sankaranarayanan–Ramasamy (SR) [16] method. This method can be used to grow single crystals along a selected crystal direction, which is very important for the preparation of functional crystals. The unidirectional solution crystallization usually occurs at around room temperature; much lower thermal stress is expected in these crystals over those grown at high temperatures [17]. From this point of view, we have attempted to grow unidirectional, bulk, good quality single crystals of BTZC from its aqueous solution by Sankaranarayanan–Ramasamy (SR) method.

In the present investigation, bulk single crystals of BTZC were grown by conventional and SR methods. The grown crystals were subjected to various studies in order to determine their properties and the results are compared with one another.

2. Experimental procedure

2.1 Conventional method

Bisthiourea zinc chloride (BTZC) was synthesized by mixing aqueous solution of zinc chloride and thiourea (99% pure) in the molar ratio 1:2. The reaction of synthesis is adhered by the equation,

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

The synthesized salt of the material was further purified by re-crystallization process using de-ionized water as solvent. The homogeneous solution obtained from the purified salt of the material is allowed to evaporate at room temperature. By spontaneous nucleation process seed crystals of well defined dimensions were obtained. Optically good quality seed crystal, free from defects was selected and kept inside the saturated solution to grow the bulk single crystal. By continuous slow evaporation of solvent at room temperature, BTZC crystal of dimension $12 \times 8 \times 2$ mm^3 have been grown with in a period of 20 days as shown in fig. 1a

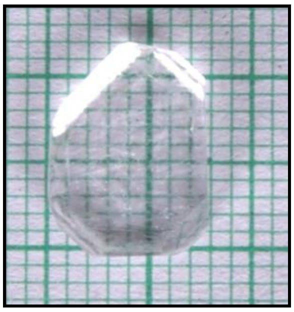

Fig. 1(a) Photograph of as conventional grown BTZC

2.2. SR method

According to the solubility data 26 g/100 ml, saturated solution of BTZC was prepared at at 316 K. Growth of BTZC crystals are carried out by conventional as well as SR method. The good transparent BTZC seed crystals were allowed to grow further to get well developed maximum size by conventional and a well faceted crystal was chosen for SR method. The morphology of the BTZC crystal has been already reported [18]. Based on the morphology of the BTZC crystal, the defect free clean surface (0 1 1) face was selected in the present study to impose the unidirectional growth. The SR method experimental set-up already reported [16, 18] consists of a heating coil, thermometer, inner container, temperature controller, growth vessel and ampoule. A ring heater positioned at the top of the growth ampoule facilitated the solvent evaporation. The assembly was designed in such a way to obtain a maximum temperature profile at the top. An optically transparent seed was fixed at the bottom of the ampoule with (0 1 1) plane at the top and filled with the saturated solution of Bisthiourea and zinc chloride. The ampoule 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. Thus, the growth is initiated from the seed fixed at the bottom of the ampoule with desired orientation. The temperature of the top and bottom portion was set as 38.5° C and 33° C, respectively for the growing crystals. The temperature around the growth region is maintained at ±0.05 $^\circ$C accuracy. The solvent is evaporated with respect to the temperature of the top portion. After few days, the seed crystal of BTZC mounted at the bottom starts to grow along the plane (0 1 1). Under this condition the highly transparent crystal was monitored and the growth system was kept constant for a long period for attaining continuous growth, which yields BTZC crystal of 64 mm length and 13 mm diameter within a period of 26 days. The photograph of the as grown crystal is shown in Fig. 2**.**

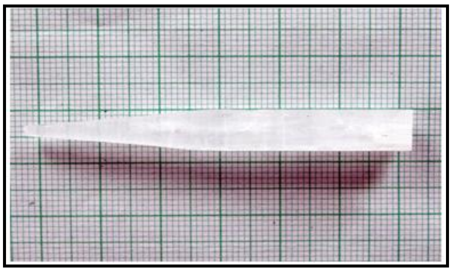

Fig. 2 Photograph of SR grown BTZC crystal

3. Results and discussion

3.1. Single crystal X-ray diffraction

The grown BTZC crystals were subjected to single crystal X-ray diffraction studies using Bruker Kappa APEX-2 diffractometer with Mo Kα (λ=0.71073 Å) radiation to determine the cell parameters and crystal structure. The result of the study reveals that BTZC crystallizes into orthorhombic system with the space group $Pn2_1a$. The lattice parameters obtained in the present study a=5.706 Å, b=12.968 Å and c=12.762 Å are in good agreement with the reported values [15].

3.2 Powder X-ray diffraction studies

Powder X-ray diffraction study was also carried out on the sample by Rich Seifert diffractometer using Cu Kα (λ=1.5418 Å) radiation. The powdered sample was scanned over the range of 2Ө values (10-70°) at a scan rate of 2° per minute. The indexed X-ray diffraction pattern obtained for BTZC is shown in Fig. 3. The well defined sharp peaks on the pattern confirm that crystallites are properly oriented without any defects. It is also pertained to note that the peak corresponding to (0 1 1) has the maximum intensity in the pattern, which evinces that the crystal is growing unidirectional axis.

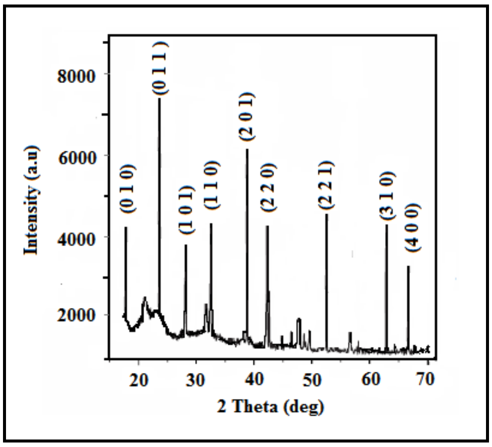

Fig. 3 Powder XRD pattern of BTZC single crystals

3.3 Optical transmission spectral studies

The transmittance of the conventional and SR method grown BTZC crystals was measured by Perkin–Elmer Lambda-35 spectrophotometer for the wavelength range of 200–1000 nm with slit width 2 nm and scan speed 240 nm/min that covers near ultraviolet, visible and higher energy part near IR region to find the transmission range to know the suitability for optical application. The UV–Vis transmittance was studied using cut and polished (0 1 1) face of SR and conventional grown BTZC crystal of 2 mm thickness. The recorded spectrum shown in Fig. 4, it is observed that the crystal transmittance percentage of SR grown crystal is 3% higher than that of the conventional grown crystal. The lower UV-cutoff wavelength is around 200 nm. The advance in percentage of transmission may be attributed to a reduced scattering from crystal's point and line defects. In order to confirm the reproducibility, the transmittance studies were repeated several times for the crystal plates cut and polished from the different parts of the grown crystals and the same results were observed. The improvement of optical transparency of SR method grown sulphanic acid, DGZC, KAP, TGS, KDP and ADP crystals has been already reported[19-22].

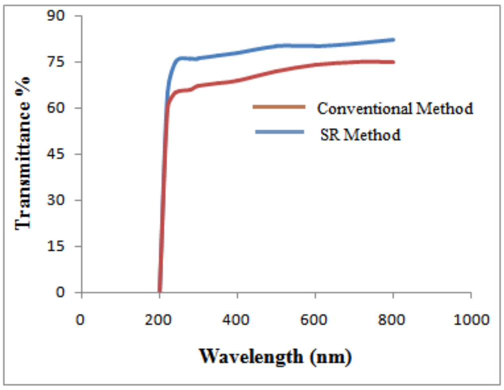

Fig. 4 Transmittance spectrum of conventional and SR grown BTZC single crystals

3.4 Vickers microhardness test

Microhardness testing is to be performed on single crystals to evaluate the mechanical properties and to examine the suitability of the material for devices by measuring the resistance of the lattice against the applied load [23]. Microhardness measurements are made on the smooth surface of the as SR and conventional grown BTZC single crystals at room temperature using LEITZ WETZLER Vickers pyramidal indentor. The load P is varied between 25 and 200 g by keeping the time of indentation constant (10 s) for all trials and the diagonal length of indentation is measured. The Vickers hardness number of the materials Hv is determined by the relation,

$$Hv = 1.8544\frac{p}{d^2}\,kg/mm^2 \qquad (2)$$

where, P is the applied load in kg and d is the diagonal length of indentation impression in mm. The variation of microhardness profile with applied load is shown in Fig. 5. From the profile it is observed that the hardness number increases with increasing load, indicating the reverse indentation size effect (RISE) [24]. The hardness number for both the crystals is measured to be 66.2 and 70.1 Kg/mm^2 respectively. The hardness for SR grown crystal was higher than hardness of conventional method grown crystal. Hardness is the resistance offered by a solid to the movement of dislocation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. Higher hardness value for SR method grown crystal indicates that greater stress is required to produce dislocations thus confirming greater crystalline perfection. BTZC single crystal grown by SR method has a good mechanical hardness, when compared to other organic NLO crystals such as DAST, DBCH, and benzophenone [25–29]. The high mechanical hardness contributes to attractiveness of the present compound in practical applications.

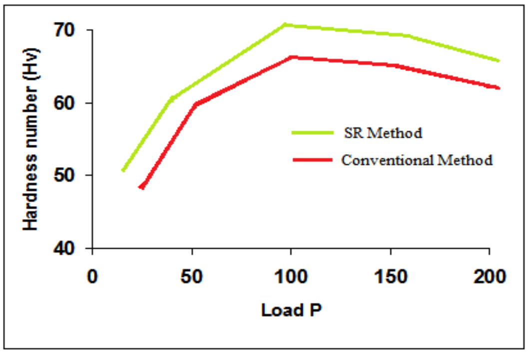

Fig. 5 Plot of Hv vs load P of conventional and SR grown BTZC single crystals

3.5. Dielectric studies

The dielectric characteristics of the material are important to know the transport phenomena and the lattice dynamics in the crystal. It also gives the information about the nature of atoms, ions, bonding and their polarization mechanism in the material. Conventional and SR method BTZC single crystals, cut in rectangular dimension was subjected to dielectric study using a HIOKI HITESTER model 3532-50 LCR meter. The surface of the sample was coated with silver paste for firm electrical contact. The experiment was carried out in the frequency range 500 Hz to 5 MHz at room temperature. The dielectric constant and dielectric loss of the crystals have been calculated using the relations,

$$\varepsilon = \frac{cd}{A\varepsilon_0} \qquad (3)$$

$$\varepsilon' = \varepsilon \tan\delta \qquad (4)$$

where, d is the thickness and A is the area of the sample respectively. The variation of dielectric constant and dielectric loss with frequency are shown in Fig.6 and 7 respectively. It is observed from the profile that both the dielectric constant and dielectric loss decrease with increase in frequency at room temperature**.** In general, the dielectric study provides information regarding the dielectric constant arises from the contribution of different polarizations mechanism, namely electronic, ionic, atomic, space charge, etc., developed in the material subjected to the electric field variations. The large dielectric constant at low frequency indicates the present of space charge polarization [30] arising at the grain boundary interface. In general, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field [31,32]. The behaviour of dielectric losses in the low frequency range depends on many factors which can be controlled (temperature rate, defects, size of crystal) [33]. Low values of dielectric loss indicate that the grown crystal contains minimum defects. [34]

The present study, in effect, indicated that high dielectric constant and low dielectric loss is obtained for the crystal grown by SR method compared to the crystal grown by conventional method. These results clearly pointed that the crystal grown by SR method has better quality than the crystal grown by conventional method.

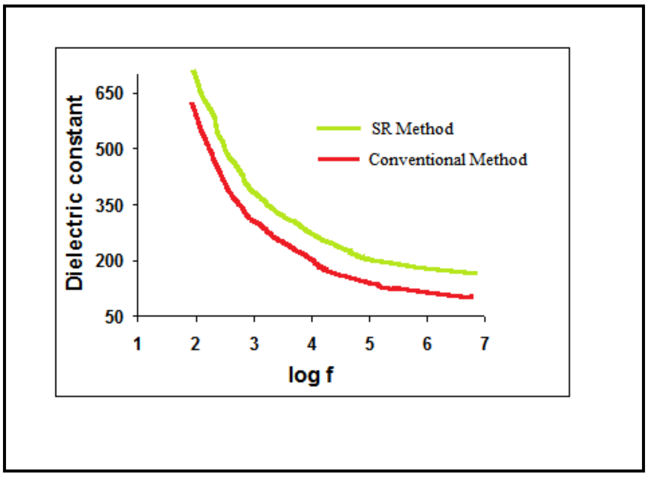

Fig. 6 Variation of dielectric constant with log f of conventional and SR grown BTZC single crystals

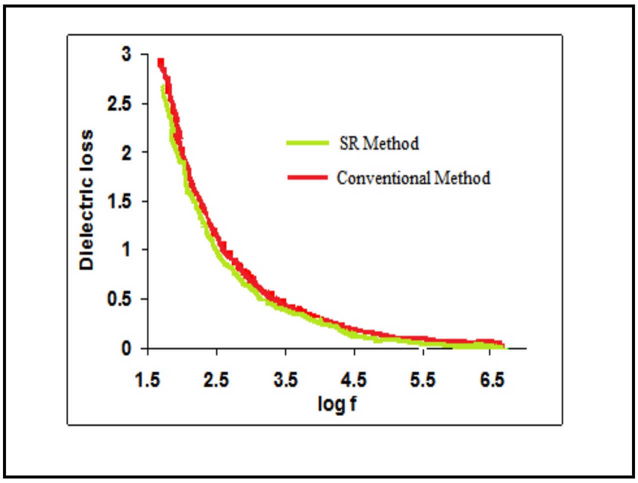

Fig. 7 Variation of dielectric loss with log f of conventional and SR grown BTZC single crystals

3.6. Laser damage threshold studies;

Most important considerations in the choice of a material for NLO applications is its optical damage tolerance and in NLO material it may severely affect the performance of high power laser systems. High damage threshold is a significant parameter for NLO material. The two similar BTZC crystals ((i) conventional slow evaporation and (ii) SR method grown) were prepared for laser damage threshold (LDT) measurements .Experimentally, a Q-switched diode array side pumped Nd:YAG laser operating at 532 nm radiation was used with 7 ns pulse width. Experimentally,a Q-switched diode array side pumped Nd:YAG laser operating at 532 nm radiation was used with 7 ns pulse width .The output from the laser was rendered to the test sample ensconced at the near focus of the converging lens .During laser irradiation ,the power meter records the energy density of the input laser beam for which the crystal gets damaged. For this measurement 32 mm diameter of the beam was focused on the crystal with 8cm focal length lens .The beam was passed along the(0 1 1)direction of BTZC for both the method grown crystals. Initially 8 mJ was employed on the surface of the Conventional grown crystal. There was a small dot formed on the sample after 40 s. For 16 mJ, the crack appeared after 8 s. In the case of SR grown crystal for 8 mJ there was no change on surface for 40 s and the small dot was formed for 10 mJ. Finally a crack was seen when applying 25 mJ for 5 s. The observed values are given in Table 1.

The laser damage threshold was calculated using the expression

$$D = \frac{E}{A}\left(\frac{GW}{cm^2}\right) \qquad (5)$$

Where D is the energy density, E is the input energy in milli joules and A is the area of the circular spot size. The calculated damage threshold for the conventional and SR method crystals are 0.3257 and 0.4673 $Gwcm^{-2}$, respectively. The high value of LDT for SR grown BTZC crystal can be attributed to the low defect content when compared with Conventional grown BTZC crystal. SR method also showed that the LDT for the SR grown benzophenone, KDP [35], benzimidazole, (DGZC) diglycine zinc chloride [36], (DMAP) dimethyl ammonium picrate[37] is higher than the Conventional grown crystal.

Table 1 Laser damage values of BTZC.

S.No	Energy (mJ)	Time(s)	Comment	
			Conventional	**SR method**
1	5	60	No change	No change
2	8	40	Small dot	No change
3	10	30	Medium dot	Small dot
4	12	10	Big dot	Medium dot
5	16	8	Cracked	Big dot
6	25	5	-	Cracked

Conclusions

Optically good quality single crystals of Bisthiourea zinc chloride have been grown using a slow evaporation solution growth technique. Also a large size (64 mm length and 13 mm diameter), unidirectional single crystal of Bisthiourea zinc chloride has been grown with a growth rate of 1.5 mm/day by the Sankaranarayanan–Ramasamy (SR) method. Single crystal XRD confirms that the crystal belongs to orthorhombic system with the space group $Pn2_1a$. Powder X-ray diffraction reveals the perfect orientation crystallite and growth of the crystal along (0 1 1) plane. The optical transmission analysis indicates that the conventional and SR method grown BTZC crystal has a wide transparency window in the visible region with a lower cutoff wavelength of 200 nm. The transmittance of the SR method grown BTZC crystal is 3% higher than the conventional grown crystal. The microhardness studies reveal high hardness value for SR method BTZC crystal and the hardness number increases as the load increases and then decreases for higher loads for both the crystals. Dielectric measurements on conventional and SR method BTZC crystals exhibit very low dielectric constant and loss at higher frequencies, indicating less defects in the samples. The laser damage threshold has been measured and the observed value for SR grown BTZC crystal is higher than that of conventional slow evaporation method grown crystal. The above results show the SR method is an efficient method to grow crystals of good perfection with good optical quality and high mechanical stability.

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