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Growth and characterization of pure and doped btzs single crystals

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Abstract: *The growth and characterization of pure and doped BTZS single crystals are discussed. In the present study powder X-Ray diffraction data of the grown crystal were recorded using BRUKER D8 Advance powder crystal X-ray diffractometer with 2.2 KW Cu anode ceramic X-ray tube. The various functional groups present in the grown crystals were identified and confirmed by recording the FTIR spectrum using BRUKER IFS-66V spectrophotometer by KBr Pellet Technique in the region 4000 – 400 cm^{-1}. The UV – Vis – NIR optical spectra of the crystals were recorded using the VARIAN CARY 5E model spectrophotometer. The degree of dopant inclusion was estimated by using Atomic Absorption Spectroscopy. The SHG efficiencies of the crystals were studied using Nd:YAG Q – switched laser.*

Keywords*: Atomic Absorption Spectroscopy, FTIR Spectrum, SHG, UV-VIS-NIR optical spectra, X-ray diffraction.*

I. Introduction

The search for novel non linear optical (NLO) crystals is gaining increased attention in recent years 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 semi organics [1-6]. The semi organic materials have the potentials for combining the high optical non linearity and chemical flexibility of organics with thermal stabilities and excellent transmittance of inorganic [7, 8]. In search of this semi organic NLO materials urea and urea analogs have been explored [9]. Single crystals of Zinc thiourea chloride (ZTC), zinc thioureasulphate (ZTS) and Bisthiourea cadmium chloride(BTCC) were grown and characterized by N.R.Dhumane[10]. J.Ramajothi et.al [11] reported the growth and characterization of tristhiourea zinc sulphate In the present work, attempts have been made to improve the physiochemical properties of BTZS with metal substitution (Cd^{2+} and Cu^{2+}). Pure and metal doped BTZS were grown and characterized by XRD, optical, thermal, mechanical, dielectric and conductivity studies.

II. Synthesis

BTZS salt was synthesized by dissolving zinc sulphate (AR grade) and thiourea (AR grade) in the molar ratio 1:2 in double distilled water. Zinc sulphate reacts with thiourea according to the reaction:

$$ZnSO_4 + 2\,[CS(NH_2)_2] \longrightarrow Zn\,[CS(NH_2)_2]_2 \bullet SO_4$$

The synthesis of Cd^{2+} and Cu^{2+} doped BTZS salts were done by replacing Zn^{2+} in BTZS by 3 mole % of Cd^{2+} and Cu^{2+} respectively. In order to obtain single crystals of high quality, purification is an important step. Hence, recrystallization was carried at least two or three times.

III. Solubility

Solubility of BTZS crystals has been determined for five temperatures 30°C,35°C, 40°C, 45°C and 50°C. Recrystalized salt is used for this purpose. A 250ml glass beaker containing 100ml of deionized water was placed in the temperature bath. The initial temperature of the bath was set at 30°C. The beaker was closed with a sheet and placed in the magnetic stirrer. The synthesized salt was added in small amount and the stirring of the solution was continued till the formation of precipitate, which confirmed the saturation of the solution. The stirring further confirmed to have uniform temperature and concentration throughout the entire volume of the solution. On reaching the saturation, the equilibrium concentration of the solution was

analyzed gravimetrically. The same procedure was repeated for the doped BTZS crystals. Figure 1 shows the solubility curves of pure, Cd^{2+} and Cu^{2+} doped BTZS single crystals.

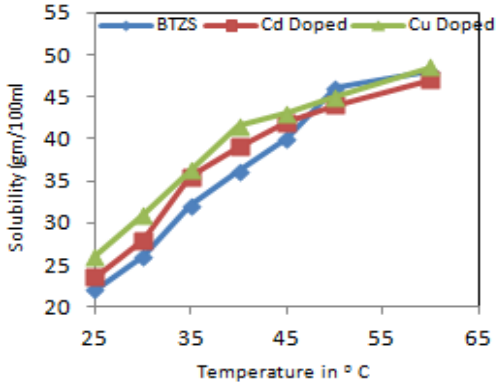

Fig. 1 Solubility curves for pure and doped BTZS

IV. Growth of pure, cd^{2+} and cu^{2+} doped btzs single crystals

Single crystals of pure, Cd^{2+} and Cu^{2+} doped BTZS were grown by slow evaporation technique at room temperature. Saturated solutions of pure and doped BTZSwere prepared using recrystallized salt at room temperature. The solutions were filtered using filter paper and kept at room temperature to evaporate the solvent. Transparent and good quality seeds were selected for the growth experiments. The period of growth ranged between 3-4 weeks. The photographs of pure and doped BTZS single crystals are shown in Fig. 2 It is seen from the photographs that both pure and doped crystals are optically highly transparent

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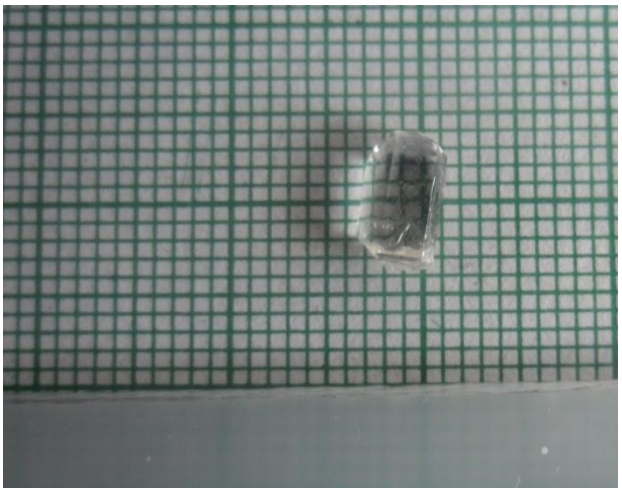
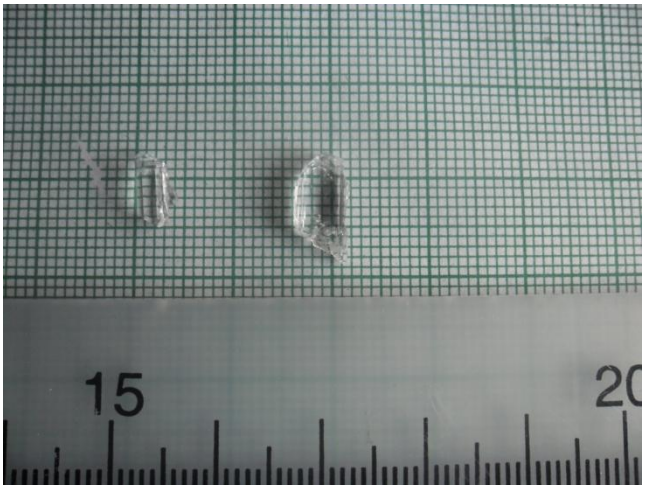
V. Characterization

5.1 X-ray diffraction studies

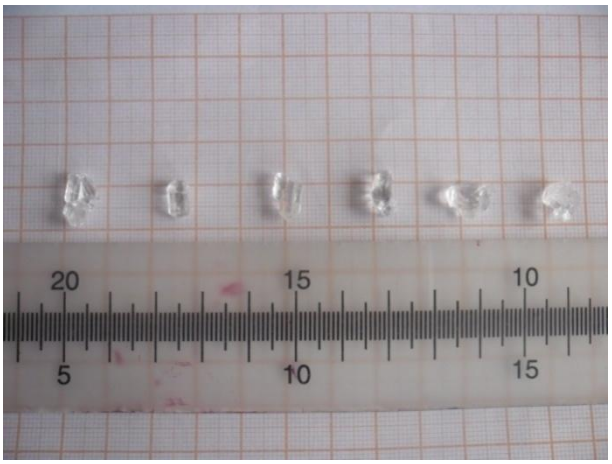
To confirm crystallinity of the grown crystals and also to determine the unit cell parameters the X-ray diffraction analysis was carried out using an X-ray diffractometer model Philips Powder X-ray diffractometer using CuKα (λ = 1.5418 A˚) . The samples were scanned over the range 20˚ to 60˚ at a scan rate of 1˚/min. The unit cell dimensions were calculated using PROSZKI software package [12]. The study revealed that BTZS crystal belongs to orthorhombic crystal system. The obtained crystallographic data are presented in the Table. 1



(a)



(b)



(c)

Fig. 2 Photographs of as grown (a) pure, (b) Cd^{2+} and (c) Cu^{2+}doped BTZS single crystals

5.2 Atomic absorption spectroscopy (AAS)

The incorporation of dopants (Cd^{2+} and Cu^{2+}) in doped BTZS crystals has been quantified by the atomic absorption spectroscopy (AAS) using a Varian AA100 Atomic Absorption Spectrometer. In order to determine the exact mole percentage of dopants incorporated in the doped crystals, crystalline powders of 110 mg of Cd^{2+} doped BTZS and 250 mg of Cu^{2+} doped BTZS were dissolved separately in 100 ml of double distilled water. These solutions were subjected to AAS. The results revealed that dopants are very low in percentile for 1 mole % metal concentrations added and they are suitably present in the crystal lattice of grown BTZS crystals.

Table. 1 Crystal data of pure and doped BTZS single crystals

Crystallographic data	Pure-BTZS	Cd^{2+}-BTZS	Cu^{2+}-BTZS
a (Å)	5.4937	5.484	5.3752
b (Å)	7.6383	8.533	8.4432
c (Å)	8.5268	7.813	7.6415
Volume $(Å)^3$	357.806	365.59	346.803
α	90º	90º	90º
β	90º	90º	90º
γ	90º	90º	90º
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic

5.3 Optical absorption studies

The optical absorption spectra of pure, Cd^{2+} and Cu^{2+} doped BTZS crystals were recorded in the range 200-2500 nm using a Varian Cary 5E model spectrophotometer. Figures 3-5 show the optical absorption spectra of pure, Cd^{2+} and Cu^{2+} doped BTZScrystals respectively. The spectra show that pure and doped BTZS have good transmission in the entire visible region. The lower cut-off wavelength lies below 250 nm.Efficient NLO crystals have an optical transparency lower cutoff wavelength between 200 and 400 nm [13].From the UV-Vis spectral analysis it is clear that there is no significant absorption in the UV and visible region thereby confirming the advantages of the crystals, the large transmission in the entire visible region and short cut off wavelength enable the crystals to be useful for second and third harmonic generation of Nd:YAG laser fundamental.The percentage of absorption of doped BTZS crystals is less than that of pure one, which is likely to improve the optical property of BTZS.

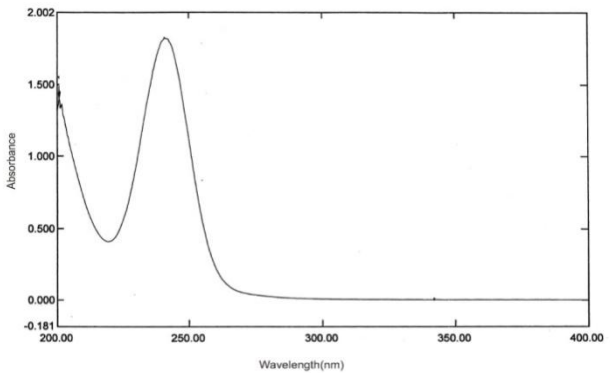


Fig. 3 The optical absorption spectrum of pure BTZScrystal

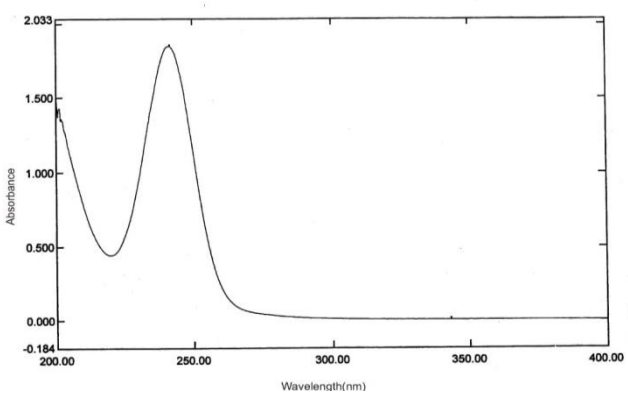


Fig. 4 The optical absorption spectrum of Cd^{2+} doped BTZScrystal

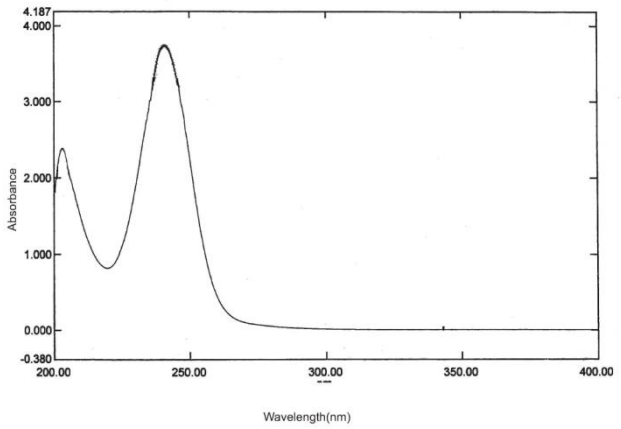


Fig. 5 The optical absorption spectrum of Cu^{2+} doped BTZScrystal

5.4 FTIR studies

Pure, Cd^{2+} and Cu^{2+} doped BTZS crystals were subjected to the FTIR studies. The various functional groups present in BTZS crystals were identified and confirmed by the FTIR study. The spectrum was recorded in the range 4000 – 400 cm^{-1} using BRUKER IFS – 66 V spectrometer, by KBr pellet technique. Figures 6-8 show the FTIR spectra of pure, Cd^{2+} and Cu^{2+} doped BTZS crystals respectively.

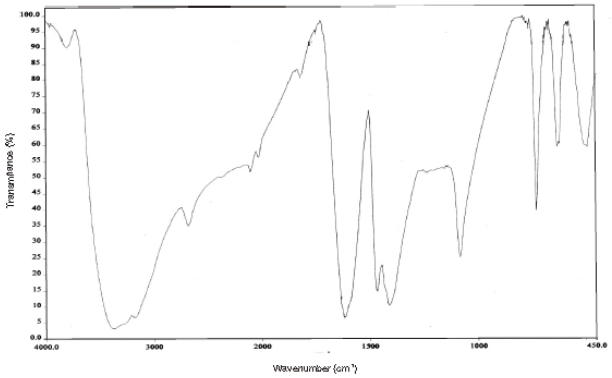


Fig. 6 The FTIR spectrum of pure BTZS crystal

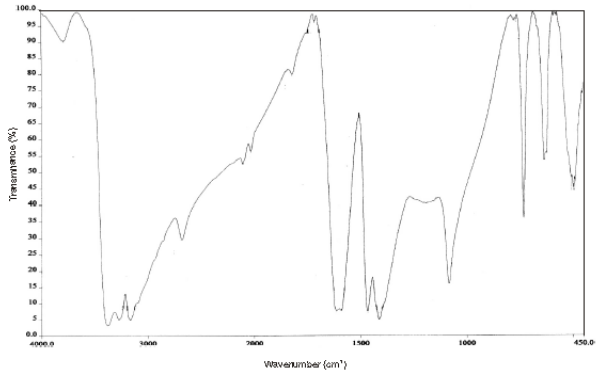


Fig. 7 The FTIR spectrum of Cd^{2+} doped BTZS crystal

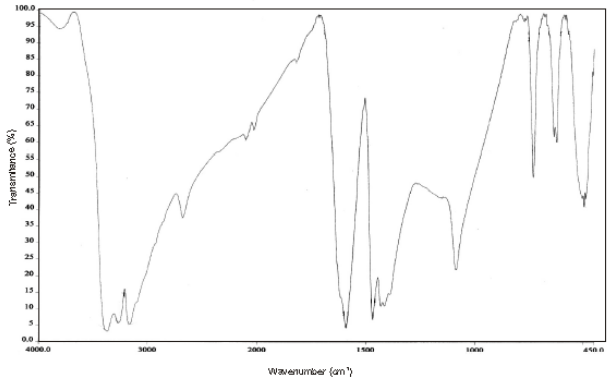


Fig. 8 The FTIR spectrum of Cu^{2+} doped BTZS crystal

Thiourea could form metal complexes by coordinate bonds through sulphur or nitrogen. Thiourea exhibits characteristic peaks at 1627, 1472, 1417, 1089, 740 and 494 cm^{-1}[14]. The band at 1627 cm^{-1} is due to NH_2 bending. The CN asymmetric and symmetric stretching vibrations are observed at 1089 and 1472 cm^{-1} respectively. The CS asymmetric stretching vibration is observed at 1417 cm^{-1}. The CS symmetric stretching is observed at 740 cm^{-1}. The band at 494 cm^{-1} is due to asymmetric NCN bending. If the bonding is through sulphur, there will be a decrease in the CS stretching frequency and an increase in the CN stretching frequency. The reverse happens if it is through nitrogen. The standard IR band frequencies of thiourea, and that obtained for pure and doped BTZS crystals are compared along with their assignments.

The CN stretching (1089 and 1472 cm^{-1}) frequencies of thiourea are shifted to higher frequencies of pure and doped BTZS (above 1046 and 1414 cm^{-1}) and CS stretching frequencies (1417 and 740 cm^{-1}) are shifted to lower frequencies of pure and doped BTZS (below 1356 and below 700 cm^{-1}). These observations suggest that the metals coordinate with thiourea through sulphur. The broad envelope positioned between 2750 and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 grouping of pure and doped BTZS crystals.

5.5 NLO Test -Kurtz Powder SHG technique

Kurtz [15] second harmonic generation (SHG) test was performed to find the NLO property of the BTZS crystals. Kurtz technique is used as a screening technique to identify the materials with the capacity for phase matching in addition to identifying the materials with non Centro -symmetric crystal structure. The crystals were ground into powder and densely packed in between two glass slides. An Nd: YAG laser beam of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation was made to fall normally on the sample cell. The emission of green light confirms the second harmonic generation of the crystals. With an energy of the 9.2 mJ of input pulses, the second harmonic signal (532 nm) of 276mW (pure BTZS), 287 mW (Cd^{2+} doped BTZS) and 294mW (Cu^{2+} doped BTZS) were obtained with reference to KDP crystal (445 mW). The experimental results indicate that the metallic dopants (Cd^{2+} and Cu^{2+}) slightly improve the SHG efficiency of the BTZS crystals.

Table. 2 Wavenumber assignment of thiourea, pure, Cd^{2+} and Cu^{2+}doped BTZS

Wavenumber (cm^{-1})				Assignment
Thiourea	Pure-BTZS	Cd^{2+}-BTZS	Cu^{2+}-BTZS	
494	488		489	(N-C-N) Asymmetric bending
740		701	700	(CS) Symmetric stretching
1089	1011	1040	1043	(CN) Symmetric stretching
1417		1356	1356	(CS) Asymmetric stretching
1472	1460	1414	1466	(CN) Asymmetric stretching
1627	1566	1630	1510	(NH_2) Asymmetric bending
3100-3300	3068	3052	3051	(NH_2) Symmetric stretching

VI. Conclusion

Single crystals of pure, Cd^{2+} and Cu^{2+} doped BTZS were grown from aqueous solutions by slow solvent evaporation method. The crystal is confirmed with X-ray diffraction analysis, the crystal belongs to the orthorhombic system. The exact percentage of metallic dopants in doped BTZS was analyzed by AAS. Optical absorption studies show that the sample is optically transparent over wide wavelength region, no absorbance and good optical transmittance in the entire visible region. The non linear optical study confirms the SHG property of the crystals. The FTIR analysis confirms the bonding interaction between zinc and sulphur atoms of thiourea molecule. The promising crystal growth characteristics and properties of BTZS crystal makes it suitable for photonic and device applications.

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