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# Effects of metal dopant ($Ba^{2+}$), optical, and mechanical studies of bisthiourea zinc chloride NLO single crystals

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ABSTRACT

Metal ion ($Ba^{2+}$) doped bisthiourea zinc chloride (BTZC) crystals are grown from aqueous solution by slow evaporation technique. The physicochemical properties and non-linear optical figure of merit are found to be improved for the grown crystals. The lattice parameters are determined by single crystal X-ray analysis. UV spectral analyses on these samples reveal the improved transparency of the doped crystals ascertaining the inclusion of metal ion in the lattice. FTIR spectral analysis carried out on the materials confirm the presence of functional groups. Microhardness studies were carried out to confirm the mechanical behavior of the crystals. Low dielectric loss shows that the grown crystal contains lesser defects authenticating the suitability of the crystal toward device applications.



## 1. Introduction

The nonlinear optical materials play crucial role in SHG, laser technology, optoelectronics, optical communications, optical data storage, optical signal processing, etc [1–6]. The key factors for material selection depend on physicochemical properties of the crystals, such as transparency range, damage threshold, the conversion efficiency, and temperature stability. Organometallic materials have the combined advantages of high optical nonlinearity and chemical flexibility of organic materials with the thermal stability and mechanical sturdiness of inorganic NLO materials [7–9]. Thiourea possesses a large dipole moment and it forms a number of coordination compounds like bisthiourea cadmium chloride (BTCC) [10] and tris thiourea zinc sulfate (ZTS) [1]. Metal ion doped semi-organic materials have excellent mechanical and thermal properties [11]. One of the requirements for a non-linear optical crystal is that it should have excellent optical quality. In recent years, many researchers have tried to find variety of NLO materials for laser applications. Non-linear optical materials utilize the non-linear dependence of the refractive index with the applied electric field [12,13]. This paper reports the crystal growth and characterization studies of pure and metal ion doped bisthiourea zinc chloride (BTZC) single crystals grown from aqueous solution by slow evaporation technique. The harvested compound is subjected to single crystal X-ray diffraction analysis and optical absorption studies. FTIR spectral analysis, microhardness studies and dielectric studies of the pure and doped grown crystals are also presented and discussed.

## 2. Experimental

### 2.1. Synthesis and crystal growth

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

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

The product was purified by repeated recrystallization before it is used for crystal growth. The doped bisthiourea zinc chloride single crystals were obtained in same molar concentration (5%) of various metal ion dopants ($Ba^{2+}$) at constant temperature of 305 K by slow evaporation technique to dimensions $16 \times 4 \times 2$, $17 \times 4 \times 3\ mm^3$ with in a period of 3 weeks. These crystals of BTZC (Figs. 1 and 2), are non-hygroscopic and optically transparent, were grown from aqueous solution.

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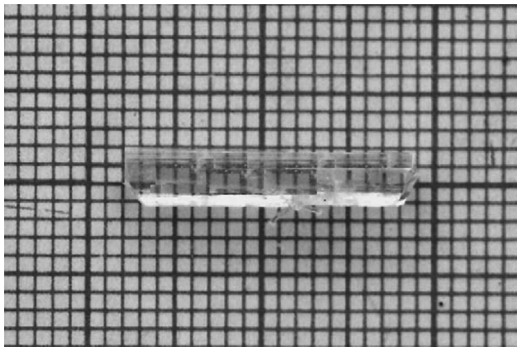

**Fig. 1.** Pure BTZC single crystal.

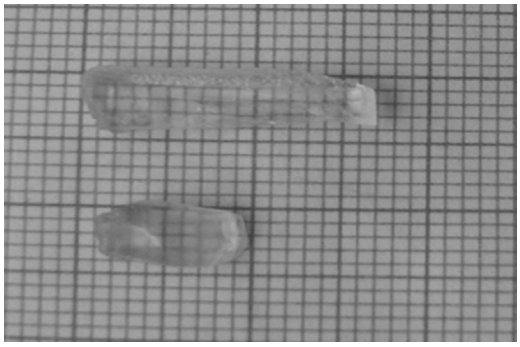

**Fig. 2.** $Ba^{2+}$ doped BTZC single crystal.

## 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 MoKα radiation (λ = 0.7170 Å) to determine the unit-cell dimensions. The pure and metal ion doped crystals are found to be crystallized in the orthorhombic system with space group $Pn2_1a$. The cell parameters are listed in Table 1. In the case of doped BTZC crystals, slight variations in the lattice parameters and cell volume values are observed. These variations may be attributed due to the incorporation of $Ba^{2+}$ ions in BTZC crystal lattice.

### 3.2. UV spectral analysis

The grown crystals of pure and doped bisthiourea zinc chloride crystals were subjected to the optical absorption studies using VARIAN CARY DRS spectrophotometer. The samples were scanned in the wavelength range 200–2000 nm. These crystals have a good transmission in the entire visible region, which is an essential property of materials for NLO applications. The UV cutoff wavelength seems to be different for ion dopants are shown in the Table 2. The UV absorption spectrum of pure and metal ion doped bisthiourea zinc chloride crystals are shown in Fig. 3 and Fig. 4, concluding that these crystals can be used for optical device fabrication.

**Table 1**
Lattice parameters of pure and ion doped BTZC single crystal.

| Sample | *a* | *b* | *c* | V(Å) |
|---|---|---|---|---|
| Pure BTZC | 5.901 | 12.752 | 12.977 | 976.513 |
| $Ba^{2+}$doped BTZC | 5.898 | 12.761 | 12.979 | 976.856 |

**Table 2**
The UV cutoff wavelengths of pure and doped BTZC crystals.

| Sample | Cutoff wavelength (nm) |
|---|---|
| Pure BTZC | 290 |
| $Ba^{2+}$doped BTZC | 310 |

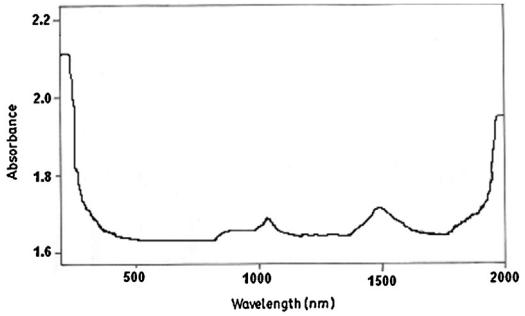


**Fig. 3.** Optical absorption spectrum of pure BTZC crystal.

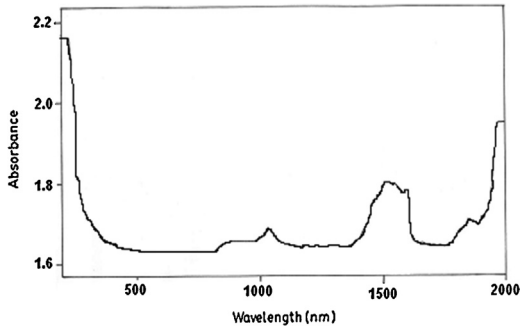


**Fig. 4.** Optical absorption spectrum of $Ba^{2+}$ BTZC crystal.

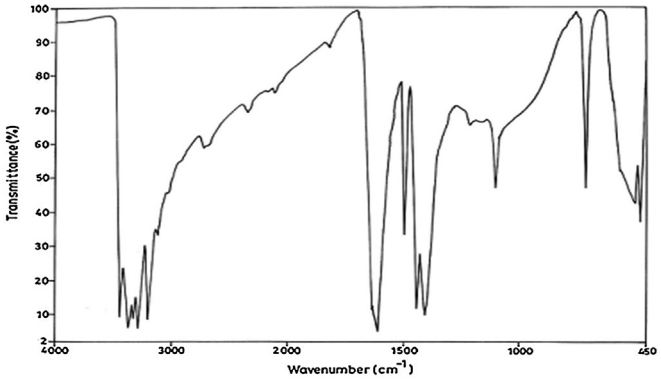


**Fig. 5.** FTIR spectrum of pure BTZC crystal.

### 3.3. FTIR spectral analysis

Fourier transform infrared transmission (FTIR) spectra of pure and metal ion doped bisthiourea zinc chloride (BTZC) crystal was carried out in the wavelength range of mid IR region, 400–4000 $cm^{-1}$. The FTIR spectrum (Figs. 5 and 6) was recorded using BRUKER IFS 66 v, in the region of 450 and 4000 $cm^{-1}$ by KBr pellet technique for its functional group confirmation and qualitative assignment. The band observed at 1633 $cm^{-1}$ is due to $NH_2$ bending. The CN symmetric and asymmetric stretching vibrations occurred at 1103 and 1496 $cm^{-1}$, respectively. The observed band at 1407 $cm^{-1}$ is assigned to CS asymmetric stretching vibration. The sharp peak appeared at 715 $cm^{-1}$ is due to the CS symmetric stretching. The peak at 477 $cm^{-1}$ is assigned to asymmetric NCN