

# Development of Novel Crystals Having Nonlinear Optical Characteristics : Thiosemicarbazide Cadmium Bromide Hydrate $\text{Cd}(\text{NH}_2\text{NHCSNH}_2)\text{Br}_2 \cdot \text{H}_2\text{O}$

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**Abstract:** *The discovery of transistor and other optical, electronic and magnetic devices motivated the major effort in crystal production and fabrication. Keeping in view, the difficulties that come across during solidification of metallic system, it was considered worth searching some transparent organic crystals in which components could be easily purified and their solidification behaviour involved low transition temperature, minimized convection effects and possibility of visual examination of the solidification process to transparency of the materials. Considering these points, the material in the present investigation has been selected.*

*X-ray powder diffraction was used to determine the crystal lattice parameters. Analysis was done by matching the X-ray line from the compound to a standard pattern. Optical transparency test was used to evaluate the grown boules. Electro-optic measurements (E.O.) was done with the original and very sensitive method. In all the observations and computations the internationally accepted current units, dimensions, notations, abbreviations and standard data have been used with the due consideration of significant figures.*

**Keywords:** Crystal growth, Optical nonlinearity, TSCCB

## I. INTRODUCTION

Extensive studies<sup>1-15</sup> have shown that conjugated organic molecules can have very large second order optical nonlinearities. These compounds exhibit extremely large nonlinear optical responses, in many cases by orders of magnitude compounds: 2-Cyclooctylamino- 5nitropyridine (COANP) and 2-(N-Prolinal)-5nitropyridine (PNP) have been shown to have a second-harmonic generation activity of atleast 1 or 2 orders of magnitude higher than those of LINBO<sub>3</sub>.<sup>16-18</sup> Further more organic materials have been found to have higher laser induced damage thresholds than inorganic materials. Typical values of 2GW/cm<sup>2</sup> for organic and 0.7GW/cm<sup>2</sup> for inorganic crystals have been reported.<sup>19-22</sup>

Experimental work was done for purification, synthesis of  $\text{Cd}(\text{NH}_2\text{HGCSNH}_2)\text{Br}_2 \cdot \text{H}_2\text{O}$  measurements of solubility, crystal growth and optical characterization of thiosemicarbazide cadmium bromide hydrate.

## II. EXPERIMENTAL

### 2.1 Materials and their purification

The chemical compounds were purified and characterised by their melting temperature before use. Organic crystals are often mechanically and thermally unstable. Therefore, attempts were made to incorporate organic molecules into complex compounds, e.g. in the form of thiosemicarbazide cadmium chloride hydrate<sup>23-24</sup>.

In the present investigation the corresponding bromide compound (TSCCB) was synthesized, crystals were grown, the crystal structure was determined and important linear and non linear optical properties of TSCCB were measured.

### 2.2. Crystal Growth:

Solution growth apparatus as is shown in fig. 2.2 in saturated solution was prepared and filtered in large covered vessel. A seed was placed to nucleate the crystal. Temperature was lowered in the range of 1-2 per 100 hours for crystal growth.

### 2.3 Measurements of Solubility:

Material is soluble in water. The accuracy of measurement was within  $\pm 0.50^\circ\text{C}$ . The experimental results are shown in Fig. (1.1)

### 2.4 Temperature Difference Technique (TDT)

Seed crystals were grown by means of a simple TDT procedure and subsequent seed growth yielded crystals of about  $(4-5) \times (4-6) \times (25-30) \text{ mm}^3$  in 4-6 weeks. The outer bath was kept at  $45^\circ\text{C}$  and the cold finger at  $38^\circ\text{C}$ .

### 2.5 Temperature-Lowering Technique (TLT):

Crystals were grown with the temperature-lowering technique between approximately  $65^\circ\text{C}$  and  $45^\circ\text{C}$ .

### 2.6 X-ray characterization:

The structure of TSCCB was determined by single crystals X-ray diffraction and structural configuration was drawn with help of the ORTEP Program 25-27.

### 2.7 Optical Characterization of TSCCB:

The Optical and nonlinear optical properties of TSCCB were investigated on a-b plane with dimensions of  $4 \times 2 \times 2.5 \text{ mm}^3$  (a**x**bxc) and c-plane with dimensions of  $4 \times 3 \times 1.8 \text{ mm}^3$ . The samples were of excellent optical quality showing homogeneous extinction over the whole crystal as shown in Fig. 1.2.

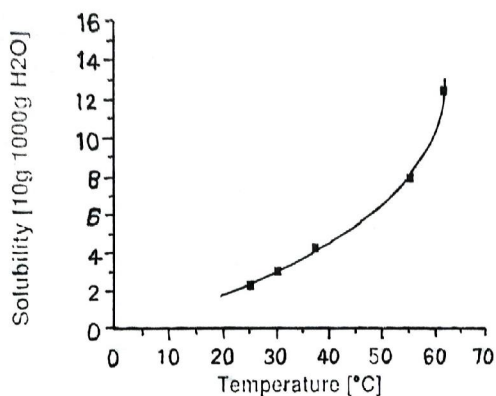


Fig.1.1 Solubility curve of Cd (NH<sub>2</sub>NHCSNH<sub>2</sub>) Br<sub>2</sub>

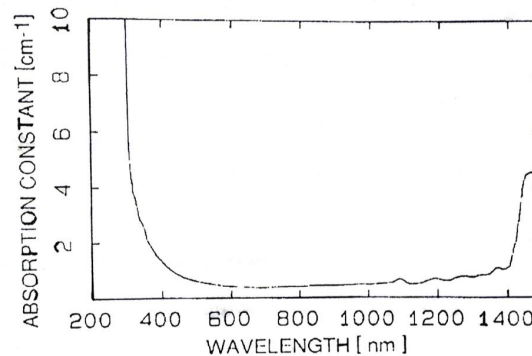


Fig.1.2 Optical absorption spectrum of a 1.8 mm thick TSCCB crystal (Light propagation parallel to a)

### III. RESULT AND DISCUSSION

#### 3.1 Purification:

The starting materials were first purified by recrystallization from aqueous solution at 600C. A saturated solution of thiosemicarbazide in water was prepared. Cadmium bromide was added to obtain nonstoichiometric 28-30 solution of 74.55wt. % CdBr<sub>2</sub> and 25.45wt % thiosemicarbazide. The solution was heated at 670C for 10 hours. By cooling this solution crystallites of TSCCB were obtained for analysis and solubility measurements as materials for subsequent crystal growth.

#### 3.2 Measurements of solubility:

Solute (TSCCB) and solvent (Water) were weighed into a glass ampoule. The ampoule was sealed and rotated in bath controlled by thermostat, the temperature of which was increased in steps of 0.50C every 1 to 2 hours. The final disappearance of the solute yielded the saturation temperature.

#### 3.3 Crystal Growth:

We have grown large single crystal TSCCB by two methods.

#### 3.4 Temperature difference technique (TDT):

Seed crystals were grown by means of a simple TDT procedure and subsequent seed growth yielded crystals of about (4-5) x (4-6) x (25-30) mm<sup>3</sup> in 4-6 weeks. The outer bath was kept at 450C and the cold finger at 380C.

#### 3.5 Temperature lowering technique (TLT):

Larger crystals were grown. Crystals of good optical quality with regular shape and a size of (5-7) x (4-6) x (30-35) mm<sup>3</sup> were grown from seed in solution at pH 2.5 in a volume of 200 ml. The cooling rate was adjusted between 100C/60-80h.

The TSCCB single crystals are shown in Fig. 1.3 All crystals had good compositional stability. Samples stored at room temperature and 60% relative humidity showed no degradation after several months. No decomposition was observed.

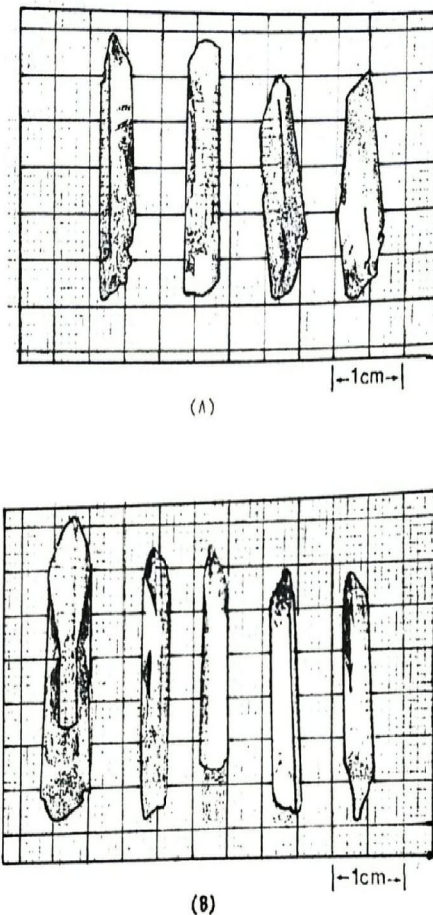


Fig. 1.3 TSCCB single crystals grown by the temperature difference technique (TDT) (A) and by the temperature lowering technique (TLT) (B)

### 3.6 X-ray Characterization:

The structure of TSCCB single crystal was determined by X-ray diffraction method. TSCCB belongs to the monoclinic space group Ia (9),  $Z=4$ ,  $a=7.063\text{\AA}$ ,  $b=14.234\text{\AA}$ ,  $C=8757$ ,

Structural data of TSCCB crystals is given in Table 1.1 at room temperature. The space group Ia was chosen to obtain  $\chi^2$  close to 900. Crystallographic data are included in Table-1. The structure consists of infinite chain of TSCCB parallel to the a direction Fig. 1.4,

Each chain element is an octahedron with a central Cd atom and vertices occupied by three Br, two S- and one N-atom. It is slightly distorted so as to accommodate the geometrical constraints of the thiosemicarbazide entity (Fig.1.5). The link between consecutive octahedra is given by one Br and One S- atom. The cohesion of the structure in the directions normal to the chain axis is due to hydrogen bonds between water molecules and the N-atoms of thiosemicarbazide. Differential-Scanning-Calorimetry (DSC) showed that TSCCB has no phase transition between 193 and 350 K.

Table -1.1: Structural data of TSCCB crystals at room temperature.

Formula	CdBr <sub>2</sub> (SCN <sub>3</sub> H <sub>5</sub> ) (H <sub>2</sub> O) (M=381.354)
Density	P = 2.93 g/cm <sup>3</sup>
Melting Point	T <sub>m</sub> = 98.50C
Space group symmetry	Ia(9) (Z=4)
Crystal class	m
Unit cell	a = 7.063 (1) Å
	b = 14.234 (4) Å
	a = 8.751 (5) Å
	β = 100.28 (2)°
Radiation	MoKα λ = 0.71069 Å

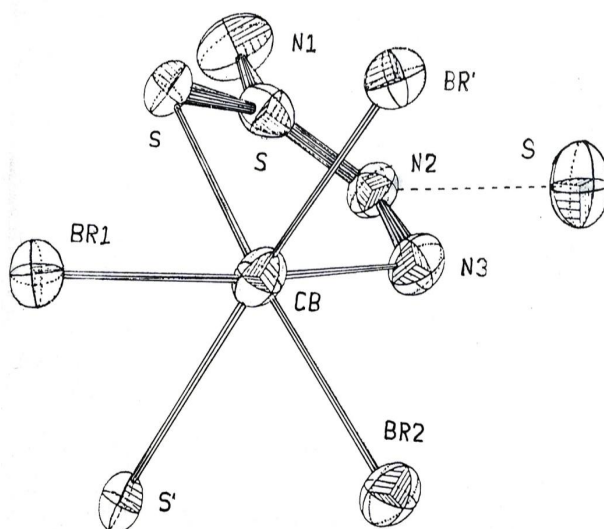


Fig. 1.4 ORTEP drawing of a single molecule of TSCCB

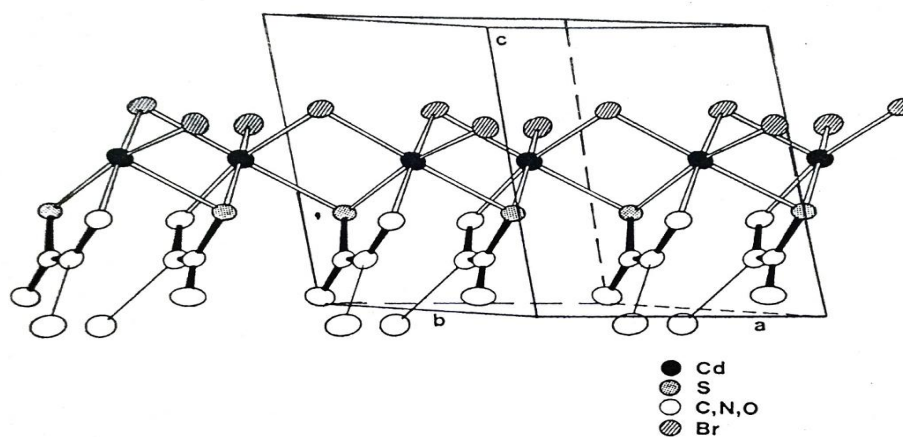


Fig. 1.5 Structure of TSCCB with unit cell (a=7.063X, b=14.234X, c=8.757 X).

For clarity only the lower layer of molecules is shown

### 3.7 Optical Characterization of TSCCB:

The optical and nonlinear optical properties of TSCCB were investigated on a b-plane with dimensions of 4 x 2 x 2.5 mm<sup>3</sup> (a x b x c) and a c-plane with dimensions of 4 x 3 x 1.8 mm<sup>3</sup>. The samples were of excellent optical quality showing homogeneous extinction over the whole crystal.

Figure 1.2, shows the absorption spectrum of a 2.5mm thick crystal for light propagation along the b axis polarized parallel to the a-c plane. The optical transmission range extends from 330 nm to 1420 nm (50% points on a 1-mm thick probe), with a minimum absorption constant.  $\alpha < 0.4 \text{ cm}^{-1}$  for  $\lambda \sim 700 \text{ nm}$ .

TSCCB is monoclinic crystal. Thus two of the main axes (A and C) of the index-ellipsoid are not parallel to the crystallographic axes. In the a-c plane the index main axes A and C are rotated with respect to the crystal axis a by an angle  $\delta$  Fig. 1.6. In the wavelength range 450-680nm,  $\delta$  is constant within 0.30.  $\delta = 17.5 + 30$

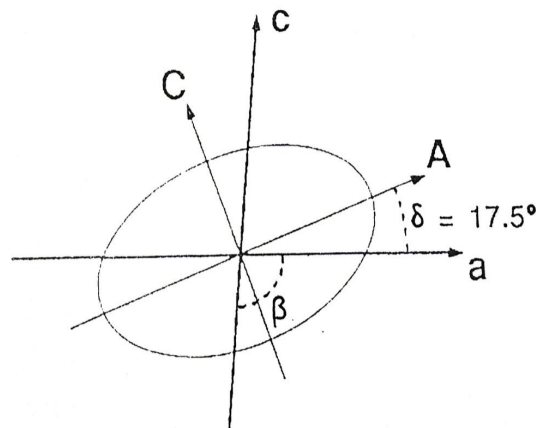


Fig.1.6 Orientation of the index-ellipsoid axes (A,B) within the crystallographic a-c plane

The refractive indices were measured by an interferometer technique. The crystal is set into one arm of a Michelson interferometric. It is then rotated around an axis perpendicular to the light beam. The change of optical path length as a function of the rotation angle is measured and used to calculate the refractive indices. The results for the wavelength  $\lambda = 633 \text{ nm}$  are

$$n_A = 1.720 + 0.01$$

$$n_B = 1.718 + 0.01$$

$$n_C = 1.812 + 0.01$$

TSCCB belongs to the point group m and the second order nonlinear optical susceptibility has ten independent nonzero elements; d<sub>11</sub>, d<sub>12</sub>, d<sub>13</sub>, d<sub>31</sub>, d<sub>32</sub>, d<sub>33</sub>, d<sub>24</sub>, d<sub>15</sub>, d<sub>35</sub>, d<sub>26</sub> (Coordinate system X<sub>2</sub> || b, X<sub>3</sub> || c and x<sub>1</sub> perpendicular to X<sub>2</sub>, X<sub>3</sub>)

The coefficients were measured on ab - plane with light polarizations parallel to A or C to avoid mixing of polarizations due to birefringence and to simplify the interpretation of the results.

The reference frame for these values is ABC  $\phi = 27.80$  is the angle between c and C.

Angle turned phase matched second harmonic generation of a Nd: YAG laser ( $\lambda = 1.06 \text{ m}$ ) has been observed by rotating ab-plane (thickness d= 2.56 mm) by an angle  $\phi = (35.0 + 0.5)^\circ$  around the C axis. The polarization pump wave was at 450 to C.

The frequency-doubled light emerged with a polarization perpendicular to C. The nonlinear susceptibility involved in this process is d<sub>15</sub>. For a peak intensity of the fundamental  $I_0 = (34 + 13) \text{ MW/cm}^2$  the conversion efficiency was 0.%. Correcting for the Fresnel reflection at the surface, the overall efficiency was determined to be 0.6%, From this value,

neglecting beam walk off, the effective nonlinear susceptibility can be estimated to be  $d_{eff} = 0.9 \text{ pm/V}$ . The accuracy of this value, however, should not be overrated.

Crystals of a new nonlinear optical material TSCCB have been grown by solution growth. Essential features of the crystal structure are present. The good optical quality of the crystal allowed the measurement of the refractive indices, absorption constants and non linear optical susceptibilities  $d_{ij}$ . Value for  $d_{ij}$  in the range of 0.3-2.8 pm/v have been determined by a Makerfringe technique. TSCCB does not show the usual  $\pi$ - electron ring, structure of most nonlinear optical organic compounds. The nonlinearity of TSCCB may be due to an organic-inorganic ring structure of the complex compound including the Cadmium ions.

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