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Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

Growth and Characterization of a Non Linear Optical Crystal - Bis Thiourea Cadmium Chloride

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ABSTRACT: Bulk crystal of bis thiourea cadmium chloride (BTCC) was grown by the solvent evaporation method and slow cooling method. The crystal structure was confirmed using single crystal XRD studies. The presence of thiourea in the complex and the metal-sulphur bond has been confirmed from the FTIR and Raman spectra. The thermal analysis shows the good stability of the crystal up to 211°C. The crystal was found to show an SHG efficiency of twice that of KDP. The surface analysis of the grown crystal was studied using AFM studies and the results are discussed in detail.

KEYWORDS: Thiourea; AFM; solution growth; non linear optical crystal.

I. INTRODUCTION

The metal–organic complexes combining the advantages of both the organic and the inorganic materials have created a great interest among the young researchers in development of many new materials having a wide application in the field of frequency conversion [1– 4]. Among the semi organic materials, complexes of thiourea are interesting because of their large nonlinear property, lower UV cut off, wide transparency and good thermal stability [5, 6]. Thiourea as a ligand possesses a large dipole moment and has the ability to form extensive network of hydrogen bonds. The well-known thiourea complex which are proved to have good SHG efficiency are bis thiourea cadmium chloride [7], bis thiourea cadmium acetate [8], bis thiourea zinc chloride [9] and bis thiourea zinc acetate [10]. This paper reports the growth of bis thiourea cadmium chloride (BTCC) by slow cooling and solvent evaporation method. The structure, thermal and optical properties of the grown crystal has been discussed in detail. The surface property was studied using AFM studies and is reported in this paper.

II. EXPERIMENTAL TECHNIQUES

The complex was synthesised by combining thiourea and cadmium chloride in the ratio 2:1 [11]. The synthesised salt was further recrystallized and was used for the bulk crystal growth. The bulk crystal of BTCC was grown using solvent evaporation and slow cooling method.The solubility of BTCC was found at different temperatures using water as a solvent. In solvent evaporation method, 500ml of the growth solution was prepared using water as solvent and the pH of the solution was optimized to 3. The solution was kept for solvent evaporation and after a growth period of 30 days bulk crystal of dimension 2.2x1.7x0.5 cm^3 was harvested. In slow cooling method, the growth solution prepared was initially kept at a temperature of 35°C and at a cooling rate of 0.1°C/day, bulk crystal of dimension 2.0x1.2x0.5 was harvested after a growth period of 30 days. Figure 1a and 1b shows the bulk crystals of BTCC by solvent evaporation and slow cooling method respectively.

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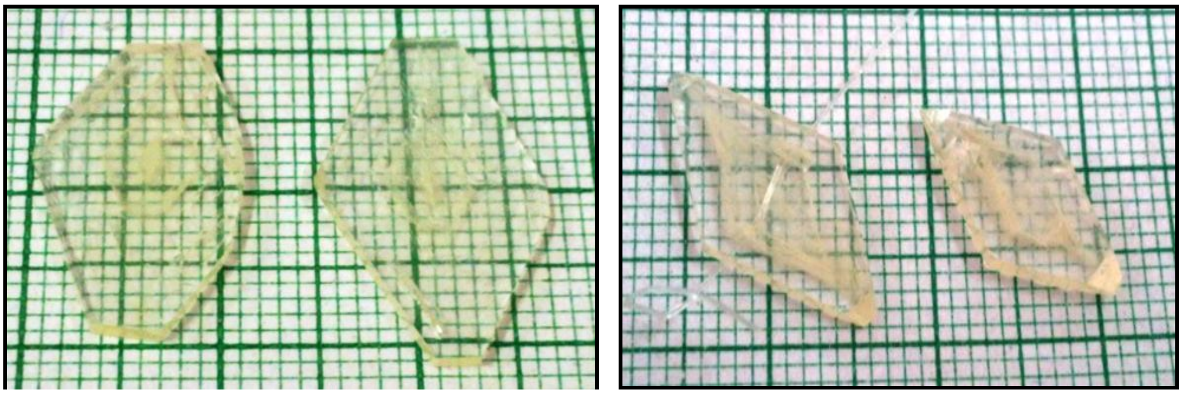


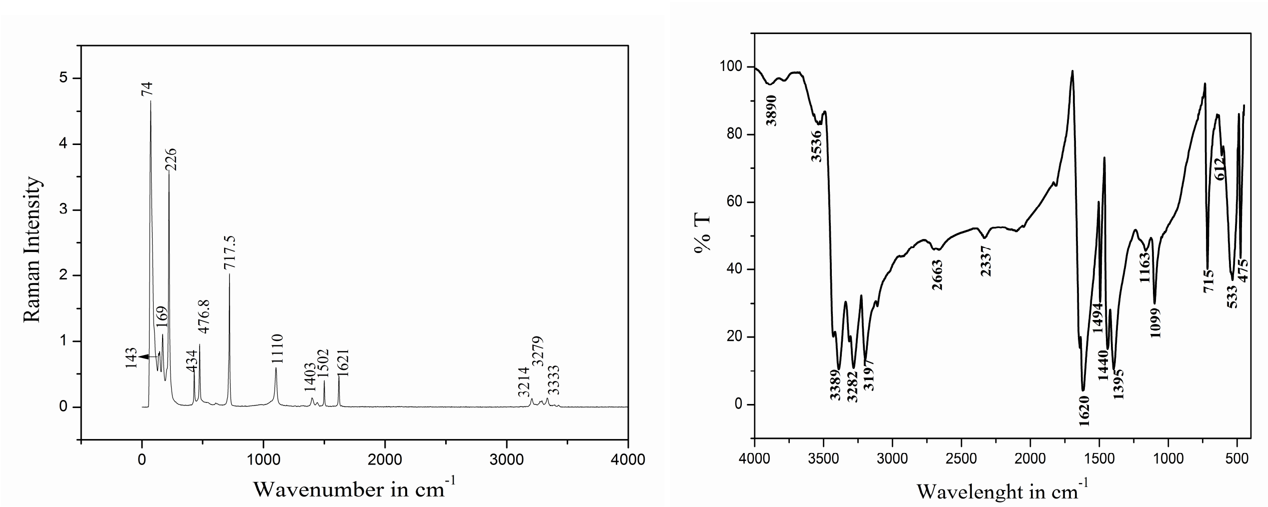
(a) (b)

Fig. 1. Bulk Crystal grown by (a) Solvent evaporation method (b) Slow cooling method

III. RESULT AND DISCUSSION

The structure of the grown single crystal was confirmed from the single crystal XRD studies. The crystal was found to crystallize in orthorhombic symmetry with the non centrosymmetric space group $Pmn_{21.}$ The cell parameters are a=5.80Å, b=6.45Å and c=13.03Å, $\alpha=\gamma=\beta=90^o$ and the volume is $487Å^3$. The cell parameters matched well with the reported values [7].

The presence of the thiourea ligand has been confirmed from the FTIR and Raman spectra. Figure 2 a and 2 b shows the FTIR and Raman spectra of BTCC respectively. Compared to pure thiourea, the symmetric stretching mode of CS group has been shifted from $730cm^{-1}$ to $715cm^{-1}$ (FTIR) and $717cm^{-1}$ (Raman) confirming metal-sulphur bonding [12]. Also a peak at $226cm^{-1}$ (R) corresponds to the Zn-S stretching vibrational mode [13]. The broad band observed in the FTIR spectrum in the range 3000 to $3400cm^{-1}$ shows the extensive hydrogen bonding in the complex [14].



(a) (b)

Figure 2.(a) FTIR spectrum of BTCC, (b) Raman spectrum of BTCC

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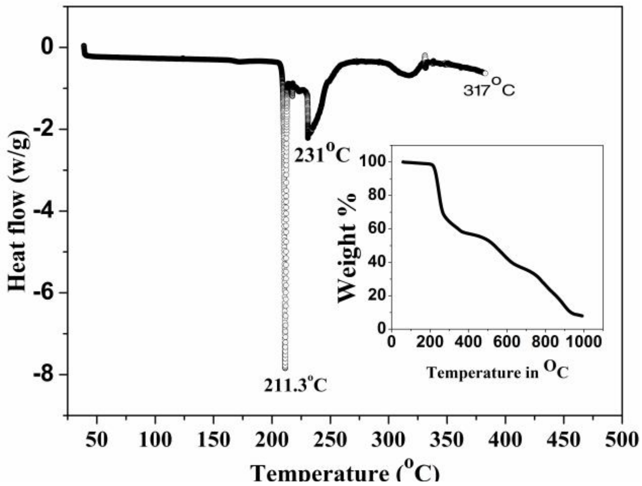
The thermal stability of BTCC was studied using TGA and DSC analysis (figure 3) and the melting point of BTCC was found to be 211°C. The complex is stable up to 211°C there after the decomposition of thiourea takes place. BTCC shows the best thermal stability compared to the other thiourea complexes.



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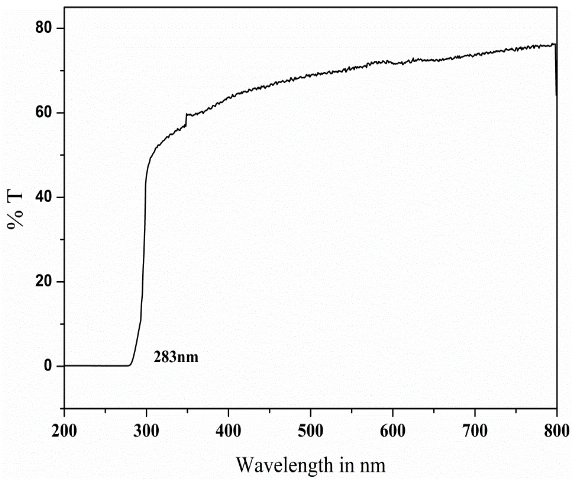

(4)

Fig. 3. DSC curve for BTCC and the inset shows the TGA curve for the complex
Fig 4. UV- Visible spectrum of BTCC

The optical transmission spectrum was recorded using Perkin Elmer Lambda 35 spectrophotometer in the wavelength range of 200–800 nm. Well-polished crystals of dimension 4mm×4mm×2mm was used for recording the spectrum. The UV spectra of BTCC crystal are shown in the figure 4. The BTCC single crystal showed a maximum transparency of 69% over the entire range of visible region. The UV cutoff wavelength was found to be 283nm. The low cut off wavelength and the transparency over the visible region make it a potential candidate for NLO applications.

The SHG efficiency of the crystal was found by Kurtz powder method and was found to be 2 times that of KDP.

The surface analysis was done by atomic force microscopy. The AFM picture of BTCC is shown in the figure 5. The picture reveals the layer growth pattern. Table 1 shows the surface parameters measured using AFM. The small pyramids like structures are the micro crystals that are distributed on the surface. The step height between the layers is also measured using AFM which was found to be 3.72nm. The surface skewness is an important parameter which is the measure of surface sharpness, If R_{ku} is less than 3 the surface is said to be very smooth whereas if it is greater than 3 then it is said to contain more peaks. The surface skewness value is negative which also confirms that the surface has more peaks than valleys [15].

TABLE 1. Parameter measured by AFM

Parameter	**BTCC**
Roughness average(R_a)nm	1.569
Root mean square (R_q)nm	2.138
Surface skewness(R_{sk})	-0.239
Surface kurtosis(R_{ku})	7.003

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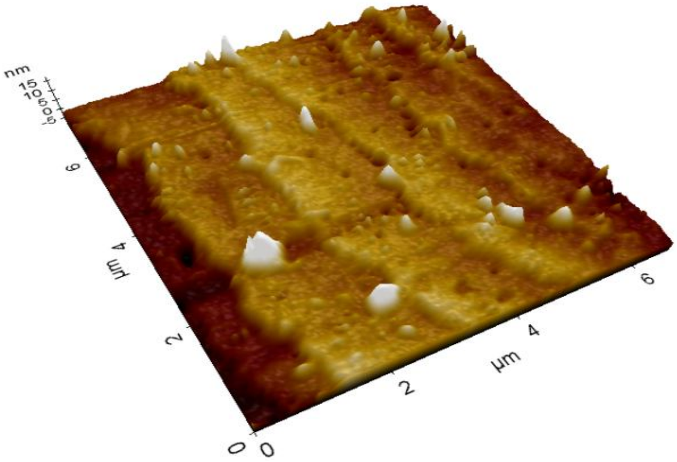

Fig. 5. AFM pictures of BTCC

IV. CONCLUSION

Bulk crystal of dimension $2.2x1.7x0.5cm^3$ and $2.0x1.2x0.5cm^3$ were successfully grown by solvent evaporation and slow cooling method. The structure of the grown BTCC single crystal was studied using single crystal analysis. The complex was found to crystallise in orthorhombic symmetry with a non centrosymmetric space group Pmn_{21}. The presence of thiourea and the coordination between the metal and the ligand are confirmed from the FTIR and Raman spectral analyses. The thermal stability of the complex was studied using TGA and DSC analysis. The complex was found to be stable up to 211^oC which is the melting point of the complex. The UV transmission spectrum shows that BTCC single crystal showed a maximum transparency of 69% in the entire visible region with UV cut-off wavelength of 280 nm. The SHG efficiency of the crystal was found to be 1.8 times that of KDP. The AFM picture shows the layer growth pattern. Thus BTCC proves to a potential candidate for nonlinear application having lower UV cut off wavelength, good SHG efficiency, good transparency in the entire range of visible region and ease growing under optimized condition.

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