Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Research Technology

Elixir Crystal Research Tech. 56 (2013) 13327-13329

ISSN: 2229-712X

Structural, thermal, optical and electrical studies of nonlinear optical tribismuthnonakisthioureanonachloride dihydrate crystal

L. Guru Prasad[1,*] and S. Sheik Saleem[2]

[1]Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, India.

[2]Department of Physics, Sri Paramakalyani College, Alwarkurichi, India.

ARTICLE INFO

Article history:

Received: 3 January 2013;

Received in revised form:

5 March 2013;

Accepted: 5 March 2013;

Keywords

Nonlinear optical crystals,
X-ray diffraction,
Thermal properties of crystalline solids,
Dielectric properties,
Ultraviolet spectra,
Photoluminescence.

ABSTRACT

Semi-organic nonlinear optical crystals of Tribismuthnonakisthioureanonachloride dihydrate has been grown by single diffusion gel growth technique. Powder XRD study reveals that the grown crystal belongs to triclinic system. Decomposition mechanism and melting point of the sample were deliberated in TGA/DSC analysis. Band gap energy value was calculated from photoluminescence spectrum. Dielectric constant of the crystal is premeditated as a function of frequency.

1. Introduction

Nonlinear optical (NLO) materials play a vital role in the field of opto- electronics and photonics [1]. Organic NLO materials have large optical coefficients but have poor mechanical stability compared to their inorganic counterparts. To setback this problem, a new hybrid materials called semi-organic materials are formed by combine both inorganic and organic materials. Semi-organic materials have large nonlinear optical property like organic materials and have high mechanical stability over organic materials [2].

In the recent years, complex of thiourea NLO crystals have attracted among the researchers [3] due to its flexibility in synthesis of a new complex. Thiourea ligand has both S and N donors; it can be coordinated either through S or N with the metal and forms a stable semi-organic complex [4]. Thiourea is an inorganic matrix modifier due to its large dipole moment and its ability to form hydrogen bonds. Centrosymmetric thiourea molecules yield noncentrosymmetric complexes when it is combined with inorganic salts [5, 6].

Metal ligand complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the coordinated metal centre. Predominant charge characteristic behavior can be observed in these metal-ligand complexes. With this reason, we have grown the tribismuthnonakis(thiourea)nonachloride dihydrate (TBNTNC) crystals and published the growth parameters, structural and vibrational behavior of TBNTNC crystal [7]. In continuation of the previous work, in this manuscript, we report, the structural, thermal, optical and electrical characterization of tribismuthnonakis(thiourea)nonachloride dihydrate (TBNTNC) crystals.

2. Experimental

Crystal growth TBNTNC crystals were grown by single diffusion gel methods. Detailed growth parameters of TBNTNC were discussed in our previous article [7]. Good quality single crystal of TBNTNC crystals were harvested over the period of 12 days.

Materials Characterization The grown crystal was characterized by powder X-ray diffraction technique, using Riche Seifert SH-37/80 diffractometer with CuKα1, radiation of 1.54059Å derived from the diffraction pattern. DSC/TGA spectrum of TBNTNC crystal was traced using SDT Q600V8.2 thermal analyzer. PL measurement of TBNTNC was taken at room temperature with 20mW, 633nm He-Ne laser was used for the excitation energy. Capacitance values of grown crystal were measured using N4L NumetricQ PSM 1735 instrument. Polished crystal of TBNTNC coated with silver paste is used to measure the capacitance.

3. Result and discussion

Powder X-ray diffraction Indexed XRD pattern of TBNTNC crystal is shown in Fig.1. Cell parameters were calculated and tabulated in Table 1. The grown crystal belongs to the triclinic crystal system and the calculated value of the cell parameters agreed with the reported structure [7] [CCDC no: 702176]. The sharp intense peaks reveals that the title compound having good crystalline nature.

Thermal analysis Fig.2. shows the TGA/DTA spectrum of TBNTNC. The recorded spectrum shows the thermal decomposition mechanism and phase transition information of the grown crystal. It is observed from the Fig.3 that there is a weight loss of about 27.43% in the region of 160 to 248^{0}C. This weight loss is attributed due to loss of two water molecules and

Tele:
E-mail addresses: guruphysics@gmail.com

thiourea molecules. Here the coordination number 8 and 4 are less stable. Coordination number 6 is an octahedral having more chelate effect than the coordination 4 and 8. Hence 4th and 8th coordinated bismuth complex can easily give up their coordinated molecules. It is clearly visible from the TGA that there is no peak above 800°C, which confirms the stability of the residue and the residue may be bismuth dimmer and bismuth oxide. Similar results have been proposed in ZTC and allylthiourea complex [8]. An exothermic peak and several endothermic peaks are traced in DSC. The endothermic peak observed at 147^{0}C with change in entropy of 47.23 J/gm. But there is no corresponding weight loss in TGA at the region 147^{0}C. This may be due to the melting of the samples.

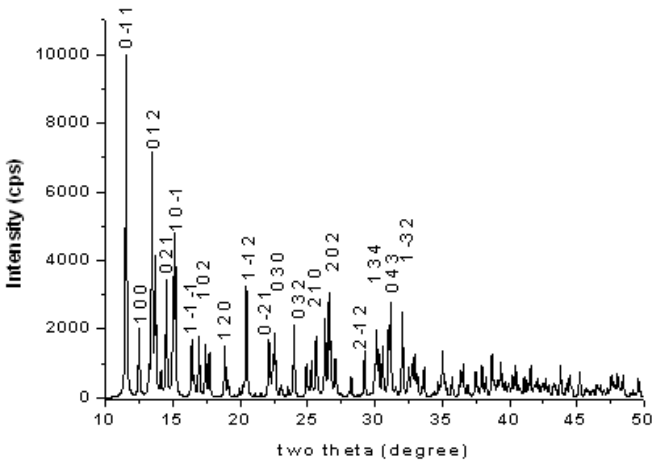

Fig.1. Powder XRD pattern of TBNTNC crystal

PL spectrum Photoluminescence (PL) studies are more preferred to detect the concentration of defects [9]. Recorded PL spectrum is shown in Fig.3. A strong emission peak is observed from the spectrum at 266 nm and it reveals that the grown crystal has UV emission property. Energy gap was calculated from the PL spectrum this emission band and the calculated value of energy gap is of 4.6642 eV. Further this UV emission band arises due to the transition of charge between nonbonding to orbital to π^* orbital from metal to ligand and also it agrees with the transmission spectrum.

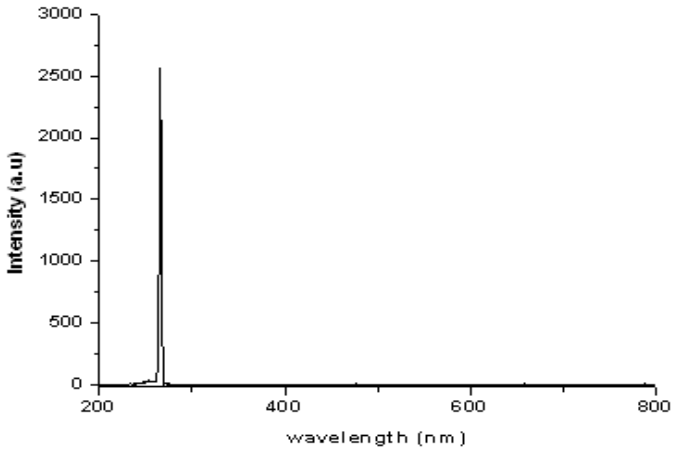

Fig.3. PL spectrum of TBNTNC crystal

Dielectric measurements Electric field distribution within the solid is investigated in the dielectric studies. Dielectric properties of NLO materials are important for their fast switching action in electro-optic applications [10]. The value of dielectric constant of the crystal was calculated using the capacitance value. It is observed from the Fig.4 that the value of dielectric constant is high in lower frequencies. This may be due to the presence of all the four types (electronic, ionic, orientational space charge) of polarization also it is decrease with increase in frequencies. The low of dielectric constant in higher frequencies side suggest the appropriateness of the grown for frequency conversion process.

Table 1. Crystallography parameters of TBNTNC crystal

Crystal Property	TBNTNC
Molecular formula	$C_9H_{40}Bi_3Cl_9N_{18}O_2S_9$
Crystal structure	Triclinic
Cell parameters	
a (Å)	7.382
b(Å)	12.212
c (Å)	13.572
α(°)	71.591
β(°)	78.921
γ(°)	82.941

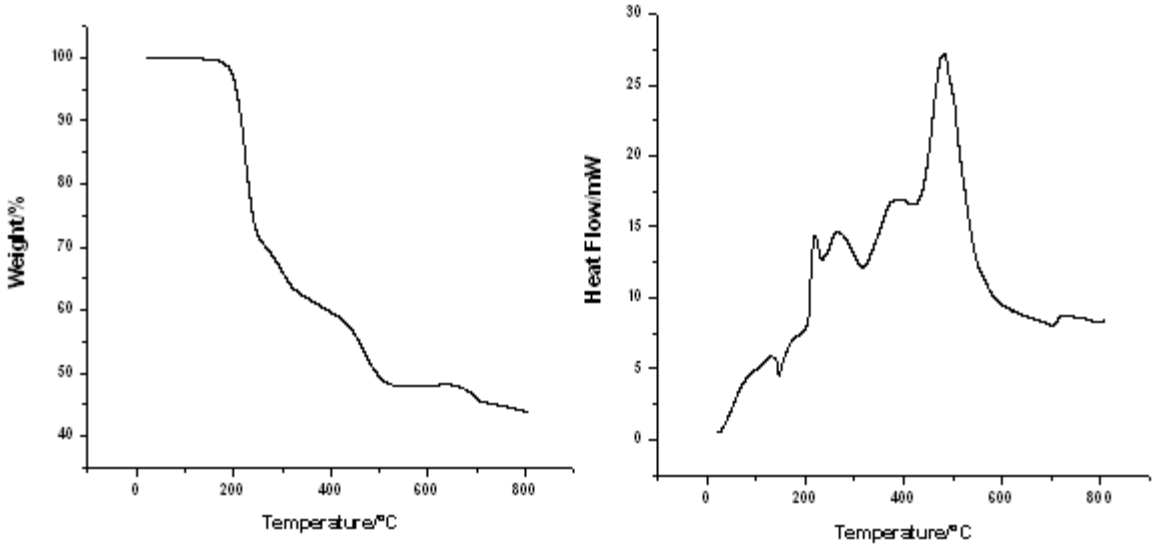

Fig 2. TGA and DSC spectrum of TBNTNC

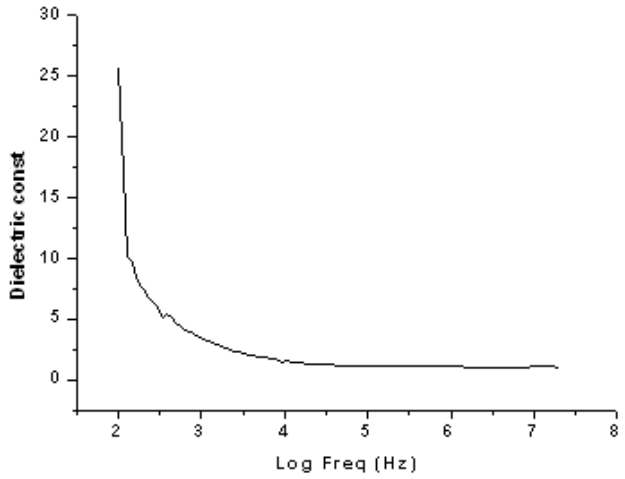

Fig.4. Plot between Log (freq) vs dielectric constant

4. Conclusion

Good quality single crystal of TBNTNC was grown by gel growth technique. Grown crystal was confirmed in XRD studies and it is crystallized in triclinic system. The DSC/TGA spectrum reveals the thermal stability of the materials and also the melting of sample is found at 147^0C. Photoluminescence spectrum indicates that the obtained crystal shows an emission band in the ultra violet region also the band gap energy was calculated. It was found that the dielectric constant value decrease with increase the frequency.

References

[1] Shiyi Guo, Duorong Yuan, Dong Xu, Guanghui Zhang, Suoying Sun, Fanqing Meng, Xinqiang Wang, Xuening Jiang, Minhua Jiang, Progress in Crystal Growth and Characterization. 2000; 40: 75-79.

[2] N. R. Dhumane, S. S. Hussaini, V. G. Dongre, P. P. Karmuse, and M. D. Shirsat, Cryst. Res. Technol. 2009; 44: 269-274.

[3] S.G.Bhat, S.M.Dharmapraksh, J. Cryst. Growth. 1997; 181**,** 390-394.

[4] A. Bhaskaran, C. M. Ragavan, R. Sankar, R. Mohankumar, and R. Jayavel, Cryst. Res. Technol. 2007; 42, 477-482.

[5] V. Kannan, N.P. Rajesh, R. Bairava Ganesh, P. Ramasamy, J. Cryst. Growth. 2004; 269, 565-569.

[6] V. Krishnakumar and L. Guru Prasad, Mater. Lett. 2009; 63, 687-690.

[7] V. Krishnakumar, S. Sheik Saleem and L. Guru Prasad J. Raman Spectrosc. 2009; 40, 1011-1015.

[8] Haiqing Sun, Duorong Yuan, Xianqrin Hou, Xinqing Wang, Liqianng Liu, Cryst. Res. Technol. 2007; 42, 65-68.

[9] S. Shahil Kirupavathya, S. Stella Marya, P. Srinivasana, N. Vijayand, G. Bhagavannarayanad, R. Gopalakrishnan, J. Crystal. Growth. 2007; 306, 102-110.

[10] Sweta Moitra, Tanusree Kar, Mater. Lett. 2008; 62, 1609-1612.