Asian Journal of Chemistry; Vol. 30, No. 2 (2018), 257-259
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2018.20869

Growth, Thermal and Spectroscopic Studies of Bis-thiourea Nickel Barium Chloride Single Crystals

RAKESH R. HAJIYANI[1,*], CHETANKUMAR K. CHAUHAN[2] and MIHIR J. JOSHI[1]

[1]Crystal Growth Laboratory, Department of Physics, Saurashtra University, Rajkot-360 005, India
[2]Department of Physics, Government Science College, Sector-15, Gandhinagar-382 016, India

*Corresponding author: E-mail: hajiyanirakesh@gmail.com

Received: 16 June 2017; *Accepted*: 29 September 2017; *Published online*: 31 December 2017; AJC-18687

Bis-thiourea nickel barium chloride was synthesized and crystals were grown by slow aqueous solvent evaporation technique. The powder XRD analysis of grown crystal was suggested to have orthorhombic crystal structure. The unit cell parameters of grown crystal as: a = 9.70 Å, b = 10.68 Å and c = 17.95 Å. The contents of nickel and barium in the grown crystals was analyzed using EDAX. The presence of various functional groups was confirmed by FTIR spectroscopy studies. From the UV-visible spectrum, the material has about 90 % optical transparency in the entire visible region. From the thermogravimetric analysis, it was found that the crystals remained stable up to 170 ºC. The endothermic reactions were identified from the differential thermal analysis.

Keywords: Bis-thiourea nickel barium chloride, Crystal growth, Slow evaporation technique, Powder X-ray diffraction.

INTRODUCTION

Non-linear optical (NLO) crystals have a great demand due to various applications in information technology and industrial applications. In previous years, organometallic materials have been attracting in the nonlinear optical field, because the flexibility available with organometallic compounds to combine the advantages of organic molecules with those of inorganic salts is very significant, which can be achieved by metal variation, ligand variation, coordination geometry, oxidation state, electron donating capability of the metal or ligand and stabilization of unstable organic fragments [1,2]. Usually, the centrosymmetric nature of thiourea molecule is combined with inorganic salt to achieve non-centrosymmetric material possessing good NLO properties. Several metal-organic complexes of thiourea materials have been designed [3,4] and synthesized several metal *bis*-thiourea complexes such as *bis*-thiourea cadmium formate [5], *bis*-thiourea cadmium chloride [6], *bis*-thiourea zinc chloride [7], *bis*-thiourea strontium chloride [8], *bis*-thiourea nickel chloride [9] and *bis*-thiourea barium chloride [10].

EXPERIMENTAL

Bis-thiourea nickel barium chloride complex was synthesized using AR grade stoichiometric incorporation of nickel chloride (0.5 M), barium chloride (0.5 M) and thiourea (2.0 M). This solution was stirred using magnetic stirrer to achieve homogenization. This homogenization solution was heated and kept for evaporation to dryness at 318 K.

Crystal growth: The synthesized salt of *bis*-thiourea nickel barium chloride was purified by repeated recrystallizations. Saturated solution of *bis*-thiourea nickel barium chloride complex was prepared at room temperature. The single crystals of *bis*-thiourea nickel barium chloride were grown by the slow solvent evaporation technique at room temperature. The colourless, transparent, platelet-type crystal of size 13 mm × 8 mm × 2.2 mm was grown after 17 days (Fig. 1).

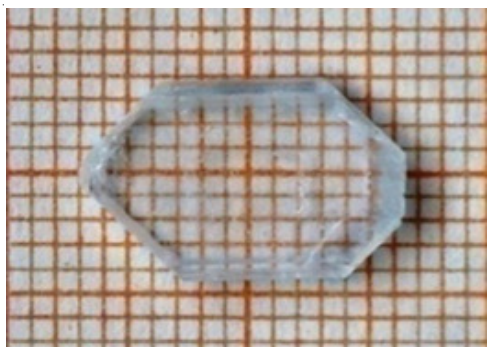

Fig. 1. Grown crystal of BTNBC

RESULTS AND DISCUSSION

Powder X-ray diffraction: The powder X-ray diffraction of *bis*-thiourea nickel barium chloride crystal was carried out on PHILIPS X'PERT MPD set-up using Cu-K_α radiation. The powder XRD pattern of *bis*-thiourea nickel barium chloride

crystal is shown in Fig. 2. The unit cell parameters were calculated using powder-X program. The estimated values of unit cell parameters of *bis*-thiourea nickel barium chloride crystals are as: a = 9.70 Å, b = 10.68 Å, c = 17.95 Å and α = β = γ = 90º, it belong to orthorhombic crystal structure.

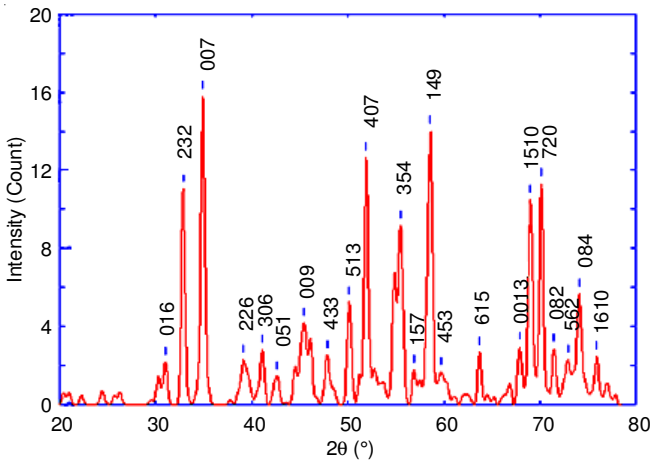

Fig. 2. Powder X-ray diffractogram of *bis*-thiourea nickel barium chloride crystal

EDAX studies: The EDAX was carried out using ZEISS EVO 18 at 20 kV. Fig. 3 shows the EDAX spectrum of *bis*-thiourea nickel barium chloride crystal. The presence of nickel and barium was confirmed by EDAX (Table-1).

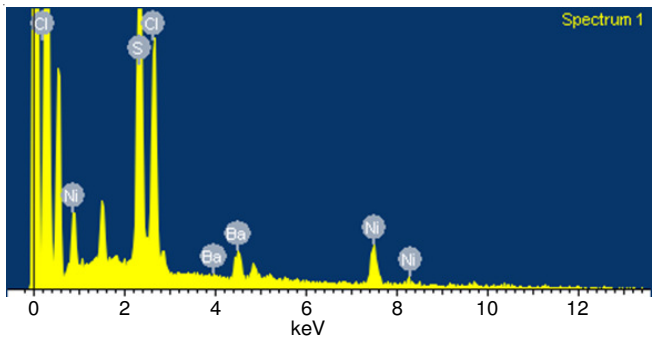

Fig. 3. EDAX spectrum of BTNBC crystal

TABLE-1
QUANTITATIVE RESULT

Element	Weight (%)	Atomic (%)
Ni	17.13	12.05
Ba	15.37	04.62

FT-IR studies: The FT-IR spectrum was recorded on SHIMADZU 8400 FT-IR spectrometer using KBr pellet in the range 3900-450 cm^{-1}. The characteristic vibrational frequencies are assigned and compared with thiourea in Table-2. The N-H absorption bands observed in the high frequency region 3400-3000 cm^{-1} in the thiourea molecule were not shifted to lower frequencies (Fig. 4) on the formation of metal-thiourea complex, thus nitrogen to metal bonds are not present and confirms the formation of metal-sulfur coordination bond [11].

Thermal studies: Thermogravimetric and differential thermal analysis were carried out using LINSEIS STA-PT 1600 in air at a heating rate of 15 ºC/min for a temperature range of

TABLE-2
COMPARISON OF FT-IR FREQUENCY
BANDS OF BTNBC WITH THIOUREA (cm^{-1})

Thiourea	BTNBC	Assignment
3380	3317	ν_{as}(N-H)
3279	3284	ν_{s}(N-H)
3177	3192	ν_{s}(N-H)
1617	1612	δ(N-H)
1477	1483	s(N-C-N)
1414	1438	σ(NH_2)
1414	1396	ν_{as}(C=S)
1082	1091	σ(NH_2)
730	717	ν(C=S)
487	491	δ(N-C-N)
457	422	ν(S-C-N)

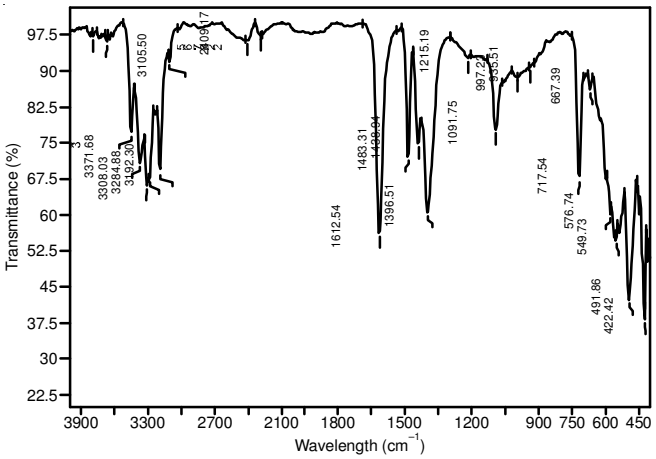

Fig. 4. FTIR spectrum of *bis*-thiourea nickel barium chloride crystal

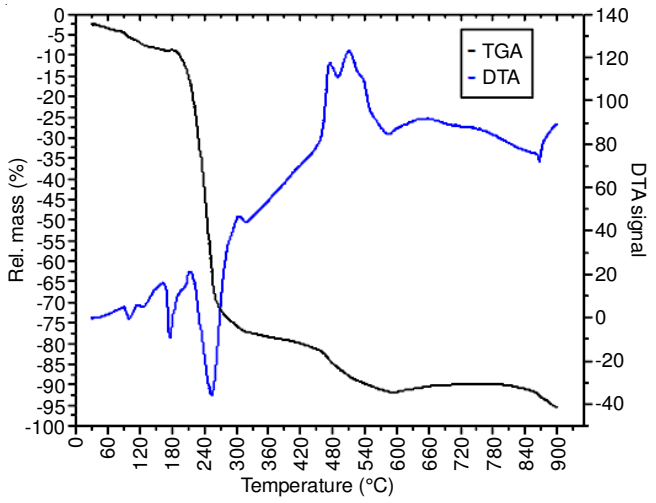

Fig. 5. TGA/DTA curve of BTNBC crystal

50-900 ºC. Fig. 5 shows the TGA and DTA traces for *bis*-thiourea nickel barium chloride crystal, which indicates that no remarkable weight loss up to 170 ºC. Lightly weight loss observed due to preparation of sample in moisturize atmosphere and becomes anhydrous then the decomposition starts precipitously. From 300 to 450 ºC a semi-stable state observed, the slow decomposition takes place and at 600 ºC onwards a stable state occurs and observed the weight loss about 91 % of the original mass. The first endothermic peak observed at 176 ºC in the DTA curve. It shows that *bis*-thiourea nickel barium

chloride crystal sample melt at 176 ºC. The second endothermic peak observed at 254.6 ºC may be due to a phase change from liquid to vapour state, which corresponds to the weight loss in TG curve.

Conclusion

The *bis*-thiourea nickel barium chloride was synthesized and its crystals were grown by slow evaporation technique. The metallic composition was assessed by EDAX and the weight percent values of nickel and barium found to be 17.13 and 15.37, respectively. The orthorhombic crystal structure with unit cell parameters was determined by powder XRD. The FTIR spectrum revealed the presence of functional groups N-H, NH_2, C=S, N-C-N and S-C-N. The *bis*-thiourea nickel barium chloride crystals were thermally stable up to 170 ºC.

ACKNOWLEDGEMENTS

The authors are thankful to UGC for financial assistance under SAP, DRS-II. The authors are also thankful to Prof. H.H. Joshi (HOD), Physics Department, Saurashtra University for his keen interest. One of authors (RRH) is thankful to Mr. H.P. Sanghvi, Deputy Director, Directorate of Forensic Science, Gandhinagar, India for the encouragement.

REFERENCES

1. J.P. Morrall, G.T. Dalton, M.G. Humphery and M. Samoc, in eds.: R. West, A.F. Hill and M.J. Fink, Advances in Organometallic Chemistry, Academic Press, Orlando, edn 1, p. 6 (2011).
2. X.Q. Wang, J.G. Zhang, D. Xu, M.K. Lu, D.R. Yuan, S.X. Xu, J. Huang, G.H. Zhang, S.Y. Guo, S.L. Wang, X. Duan, Q. Ren and G. Lu, *J. Cryst. Growth*, **235**, 340 (2002); https://doi.org/10.1016/S0022-0248(01)01811-5.
3. P.M. Ushasree, R. Muralidharan, R. Jayavel and P. Ramasamy, *J. Cryst. Growth*, **218**, 365 (2000); https://doi.org/10.1016/S0022-0248(00)00593-5.
4. K. Selvaraju, R. Valluvan and S. Kumararaman, *Mater. Lett.*, **61**, 751 (2007); https://doi.org/10.1016/j.matlet.2006.05.054.
5. P. Sagayaraj and S. Selvakumar, *J. Mater. Sci. Mater. Electron.*, **20(S1)**, 299 (2009); https://doi.org/10.1007/s10854-008-9592-6.
6. V. Venkataramanan, S. Maheswaran, J.N. Sherwood and H.L. Bhat, *J. Cryst. Growth*, **179**, 605 (1997); https://doi.org/10.1016/S0022-0248(97)00137-1.
7. L.R. Nirmala and J.T.J. Prakash, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **110**, 249 (2013); https://doi.org/10.1016/j.saa.2013.03.050.
8. R.R. Hajiyani, D.J. Dave, C.K. Chauhan, P.M. Vyas and M.J. Joshi, *Mod. Phys. Lett. B*, **24**, 735 (2010); https://doi.org/10.1142/S0217984910022810.
9. C. Ramachandraraja, A.A. Joseph, R.S. Sundararajan, V.S. Shankar and P. Murugakoothan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **74**, 1005 (2009); https://doi.org/10.1016/j.saa.2009.07.007.
10. M.M. Kumari, P.I. Ramachandran, C. Ravikumar, I.H. Joe and I. Nemec, *J. Raman Spectrosc.*, **42**, 1462 (2011); https://doi.org/10.1002/jrs.2854.
11. K. Nakamoto, IR Spectra of Inorganic and Coordination Compounds Wiley & Sons, New York, edn 2 (1978).