Spectroscopic Investigation on fundamental modes of pure and doped BTMC NLO single crystals

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 ABSTRACT

Thiourea is potentially capable of forming coordinate bonds through both sulphur and nitrogen even though the extremely low basicity of the ligands militates against the formation of nitrogen-metal bonds. Both these possibilities will be reflected in the infrared spectra of the complexes. The centrosymmetric thiourea molecule when combined with inorganic salts yields non-centrosymmetric complexes, which has non linear optical properties. In the present study optically transparent crystals of Pure and doped BTMC crystals have been grown. The crystals are characterized by subjecting to Powder XRD, AAS, FTIR, UV and SHG tests are discussed and values tabulated.

Keywords: NLO, XRD, FTIR, AAS, UV, BTMC, SHG

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INTRODUCTION

Second order nonlinear optics continues to be a topical area of research because of its tremendous potential in the design of photon-based new materials for optical switching, data manipulation and information processing [1-4]. Materials with large second-order optical nonlinearities, lower cut-off wavelength and stable physicochemical performance are needed in order to realize many of photonic and optoelectronic applications. Considerable efforts are made to develop new organic materials with large second-order nonlinear optical (NLO) susceptibilities. Most commercial materials especially for high power are inorganics. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long term promise than inorganics. A variety of materials have been investigated for their nonlinear optical properties, e.g., inorganic materials, organic molecules, polymer, liquid crystals and organometallic compounds. Inorganic materials are much more matured in their application to second order NLO materials than organics. They posses large non linearity, high resistance laser induced damage and low angular sensitivity [5, 6]. Bis(thiourea) magnesium chloride (BTMC) is a good candidate for engineering, a material with high nonlinearity out of an organic ligand by metal complexation. Special features of these crystals are that they have an extended transparency down to UV, high optical nonlinearity and good mechanical property. The main objective of the present work is to improve the physicochemical properties of BTMC by substituting metallic dopants (Cd^{2+} and Zn^{2+}).

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1. **SYNTHESIS**

Bis(thiourea) magnesium chloride salt was synthesized by mixing aqueous solutions of magnesium chloride (AR grade) and thiourea (AR grade) in the molar ratio 1:2. The chemical reaction is:

$$MgCl_2 + 2 [CS (NH_2)_2] \longrightarrow Mg [CS(NH_2)_2]_2 \bullet Cl_2$$
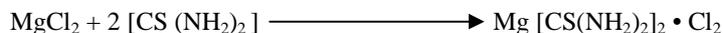
The Cd^{2+} and Zn^{2+} doped BTMC salts were also synthesized by replacing Mg^{2+} in BTMC by 3 mole % of Cd^{2+} and Zn^{2+} respectively. The synthesized salts were dissolved in double distilled water and purified by repeated recrystallization. The single crystals of as grown crystals of pure and Cd^{2+} and Zn^{2+} doped BTMC are shown in figures 1.1 (a), (b) and (c) respectively.

2. **CHARACTERIZATION OF PURE, Cd^{2+} AND Zn^{2+} DOPED BTMC SINGLE CRYSTALS**

In the present work, the grown crystals of pure and doped BTMC were subjected XRD to confirm the crystal structure, AAS to quantitatively analyze the incorporation of metal ions in the crystal lattice, Optical transmission studies to estimate the UV cut–off wavelength and transmission range, FTIR studies to ascertain the metal coordination and the presence of various functional groups, NLO test to confirm the second harmonic generation (SHG).

Fig. 1.1 (a) Photographs of as grown Pure BTMC single crystals

Fig. 1.2 Photographs of as grown Cd^{2+} doped BTMC single crystals

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Fig. 1.3 Photographs of as grown Zn^{2+} doped BTMC single crystals

3.1 X-RAY DIFFRACTION ANALYSIS

Single-crystal diffractometers are most often used to determine the molecular structure of new materials. Powder diffractometers are routinely used for phase identification and quantitative phase analysis but can be configured for many applications, including variable-temperature studies, texture and stress analysis, grazing incidence diffraction, and reflectometry. The powder diffraction of a substance is characteristic of the substance and forms a sort of fingerprint of the substance to be identified. The peaks of the X-ray diffraction pattern can be compared with the standard available data for the confirmation of the structure. For the purpose of comparison, many standards are available, some of which are, Willars Hand book, Joint Committee on Powder Diffraction Standards (JCPDS) and National Bureau of Standards. The unit cell parameters of pure, Cd^{2+} and Zn^{2+} substituted BTMC single crystals are presented in Table 1.1. It is observed from the table that the cell parameters and the volume of the Cd^{2+} and Zn^{2+} doped BTMC crystals slightly differ from those of the pure BTMC, which may be attributed to the presence of Mg^{2+} and Zn^{2+} dopants in BTMC crystals. Both pure and doped crystals are found to be orthorhombic in structure. The XRD results suggest that the presence of dopants has not altered the basic structure of the crystal.

Table 1.1 Crystal data of pure and doped BTMC single crystals

Crystallographic data	Pure-BTMC	Cd^{2+}-BTMC	Zn^{2+}-BTMC
a (Å)	5.1651	5.17624	5.00262
b (Å)	5.8509	5.76097	5.57194
c (Å)	11.8332	11.6679	11.28922
Volume (Å^3)	448.83	439.3485	425.5022
A	90º	90º	90º
B	90º	90º	90º
Γ	90º	90º	90º
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic

3.2 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic absorption spectroscopy (AAS) determines the presence of metals in liquid samples. Metals include Fe, Cu, Al, Pb, Ca, Zn, Cd, Mg and many more. It also measures the concentrations of metals in the samples. Cd^{2+} doped BTMC and Zn^{2+} doped BTMC single crystals were dissolved separately in 100 ml of double distilled water and then subjected to AAS analysis. The AAS results revealed that 1.2 % and 1.56 % of dopants present in the BTMC crystals respectively.

3.3 UV-Vis-NIR SPECTROSCOPY

UV-Vis-NIR spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons

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involved are usually the outer valence or bonding electrons, which can be excited by absorption of UV or visible or near IR radiation. Excitation of a bound electron from the Highest Occupied Molecular Orbital increases the spatial extent of the electron distribution, making the total electron density larger and more diffuse, and often more polarizable. A vibrational excited state of the molecule contains rotational excitation and electronic excited state of a molecule also contains vibrational excitation.

The optical absorption spectra of pure and doped BTMC have also been recorded in the region 200-800 nm using Varian Cary 5E Model spectrophotometer. The UV-Vis-NIR absorption spectra of pure, Cd^{2+} and Zn^{2+} doped BTMC single crystals are shown in Fig. 2.1, Fig. 2.2, and Fig. 2.3 respectively.

Absorption in the near ultraviolet region arises from electronic transitions associated with the thiourea units of BTMC. In BTMC, the thiourea units within the structure are nearly coplanar and it is a resonance hybrid of three resonance structures with each contributing roughly in an equal amount. The π-orbital electron delocalisation in thiourea, which arises from the mesomeric effect, is responsible for their nonlinear optical response and the absorption in near ultraviolet region. [7-10]

In all the three spectra, it is found that both pure and doped BTMC crystals have a low UV cut-off wavelength lying at 245 nm with very low absorption in the visible region. It is also observed that the percentage of absorption of doped ones is less than that of pure ones.

The percentage of transmission is very high for the three samples, which is a required property for NLO materials. In addition, the higher percentage of transmission for doped ones in comparison to pure BTMC, is likely to improve the enhancement of NLO property
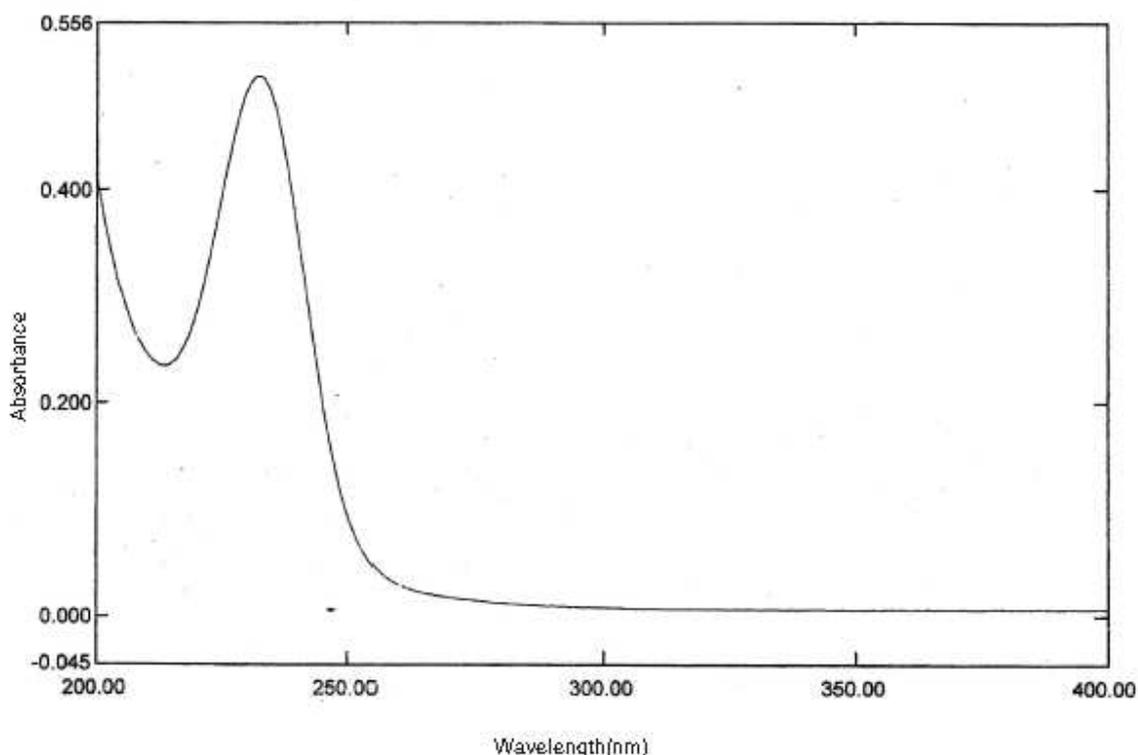

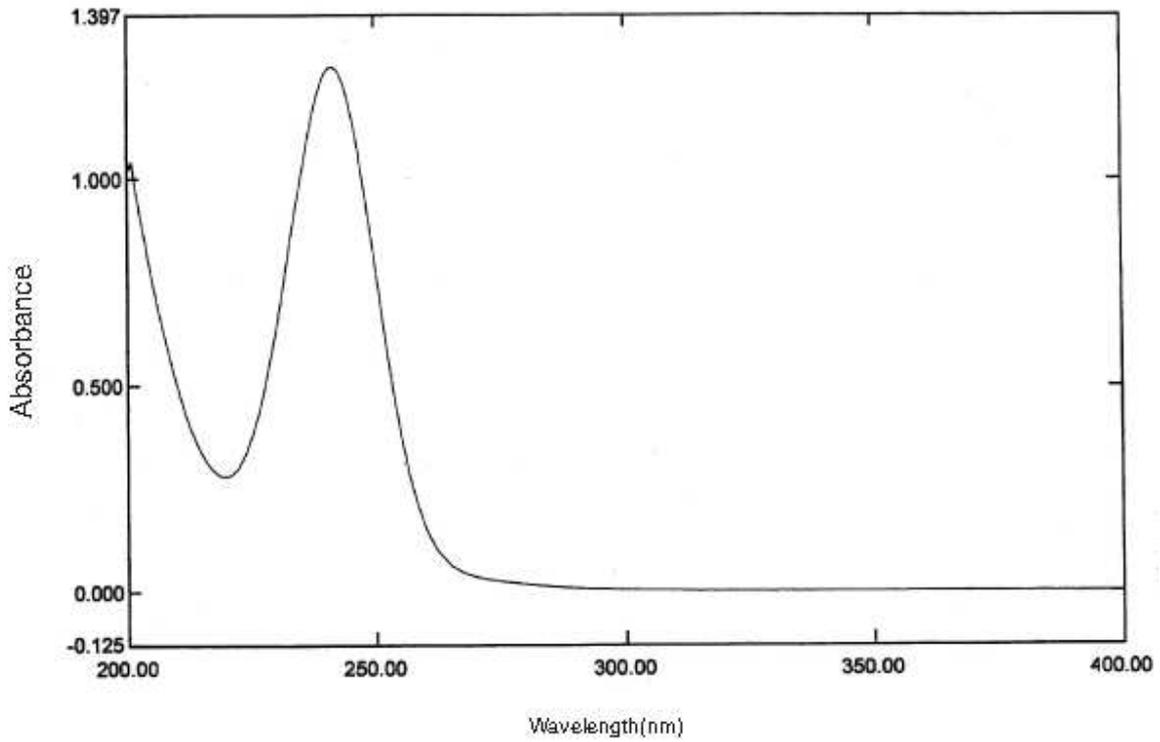**Fig. 2.1**   **The UV-Vis-NIR absorption spectra of pure BTMC single crystal**

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Fig. 2.2   **The UV-Vis-NIR absorption spectra of Cd²⁺ doped BTMC single crystal**
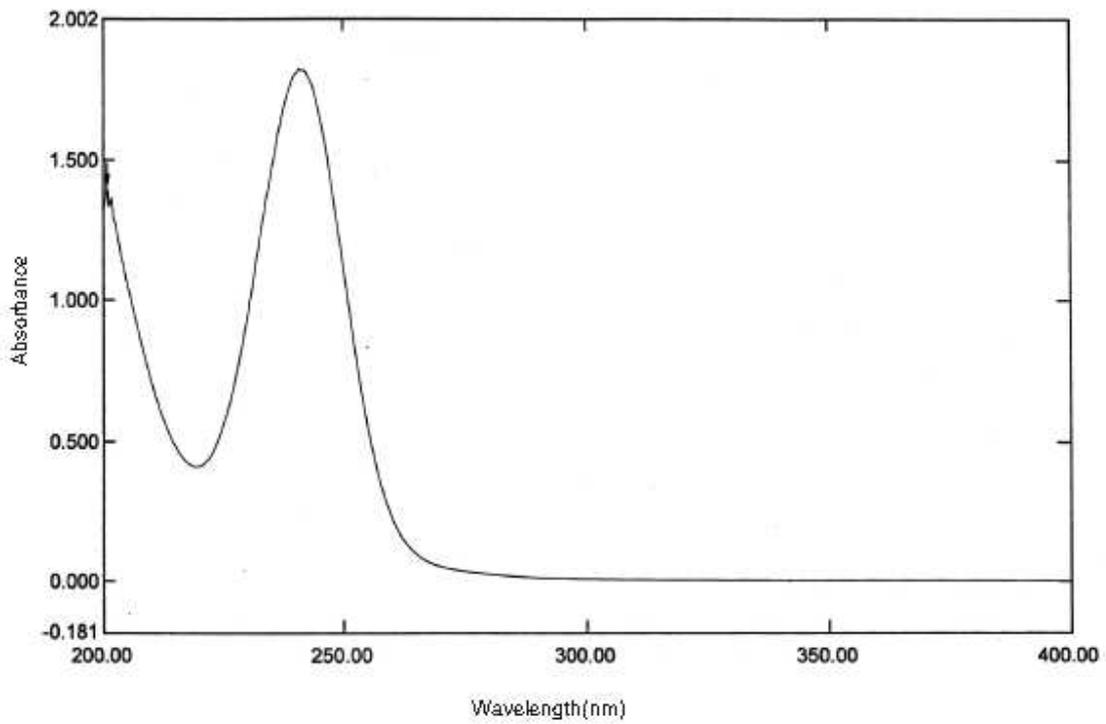

Fig. 2.3 - The UV-Vis-NIR absorption spectra of Zn²⁺ doped BTMC single crystal

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3.4 FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS

Thiourea is potentially capable of forming coordinate bonds through both sulphur and nitrogen even though the extremely low basicity of the ligand militates against the formation of nitrogen – metal bonds[11]. Bonding through the sulphur would increase C-N stretching frequency. Bonding through the nitrogen would produce the opposite effect. Further, N-H frequency should decrease if the metal is coordinated through nitrogen, while remaining unaffected if the bonding is through sulphur [12].

The FTIR spectra of pure, Cd^{2+} and Zn^{2+} doped BTMC crystals are presented in Fig. 3.1, Fig. 3.2 and Fig. 3.3 respectively. Different groups of vibrations of these materials are compared with thiourea and presented in Table 2.2.

The thiourea crystal exhibits the bands in the region $400 – 750$ cm^{-1}, $1050 – 1150$ cm^{-1} and $1300 – 1650$ cm^{-1} These bands arise due to the strong coupling between C=S, C-N and $\delta(NH_2)$ vibrations, respectively. The very strong vibrational lines observed at 740 and 1417 cm^{-1} in FTIR spectrum are due to the CS symmetric and asymmetric stretching vibration modes respectively. The strong peaks at 1089 and 1472 cm^{-1} have been assigned to CN symmetric and asymmetric stretching vibrational modes. The intense peak at 1627 cm^{-1} is due to NH_2 asymmetric bending vibrations. The high wave number region $(3100 – 3400$ cm$^{-1})$ arises due to NH stretching vibrations. The thiourea crystal exhibits the bands in the region 400-750 cm^{-1}, 1050-1150 cm^{-1} and 1300-1650 cm^{-1}. These bands arise due to the strong coupling between C=S, C-N and $\delta(NH_2)$ vibrations respectively. The asymmetric NCN bending is observed at 494 cm^{-1}. The very strong vibrational lines observed at 740 and 1417 cm^{-1} in FTIR spectrum are due to the CS symmetric and asymmetric stretching vibrational modes respectively. The very strong peaks observed at 1089 and 1472 cm^{-1} have been assigned to symmetric and asymmetric stretching of vibrational modes of C-N respectively. The intense peak at 1627 cm^{-1} is due to NH_2 asymmetric bending vibration. The high wavenumber region (3100-3400 cm^{-1}) arises due to the N-H stretching vibrations. These vibrational assignments were taken into account in assigning the FTIR bands in pure and doped BTMC crystals.

Table 2.2 Wavenumber assignment of thiourea, pure, Cd^{2+} and Zn^{2+} doped BTMC

Wavenumber (cm^{-1})				Assignment
Thiourea	Pure-BTMC	Cd^{2+}-BTMC	Zn^{2+}-BTMC	
469	451		430	(N-C-S) Symmetric bending
494	490		486	(N-C-N) Asymmetric bending
740	702	730	729	(CS) Symmetric stretching
1089	1114	1083	1086	(CN) Symmetric stretching
1417	1380	1413	1412	(CS) Asymmetric stretching
1472	1491	1473	1473	(CN) Asymmetric stretching
1627	1600	1618	1621	(NH$_2$) Asymmetric bending
3100-3300	3255	3277	3283	(NH$_2$) Symmetric stretching

The CS stretching (1417 cm^{-1}) vibration of thiourea is shifted to lower values of pure (1380 cm^{-1}), Cd^{2+} (1413 cm^{-1}) and Zn^{2+} (1412 cm^{-1}) doped BTMC. This clearly indicates the coordination of sulphur with metals. The CN stretching (1089 cm^{-1}) vibration of thiourea is shifted to higher values of pure (1114 cm^{-1}), Cd^{2+} (1083 cm^{-1}) and Zn^{2+} (1086 cm^{-1}) doped BTMC. This clearly establishes the delocalisation of nitrogen lone pair electron over carbon sulphur double bond, which is an essential property for NLO materials.

The absorption bands observed at 1600 cm^{-1} (pure BTMC), 1618 cm^{-1} (Cd^{2+} doped BTMC) and 1621 cm^{-1} (Zn^{2+} doped BTMC) are assigned to the NH_2 asymmetric bending vibrations. The broad envelope positioned between 2750 and 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 grouping of BTMC crystals. The non-shifting of NH vibration bands indicates that the metal is not coordinated through nitrogen, but through sulphur.
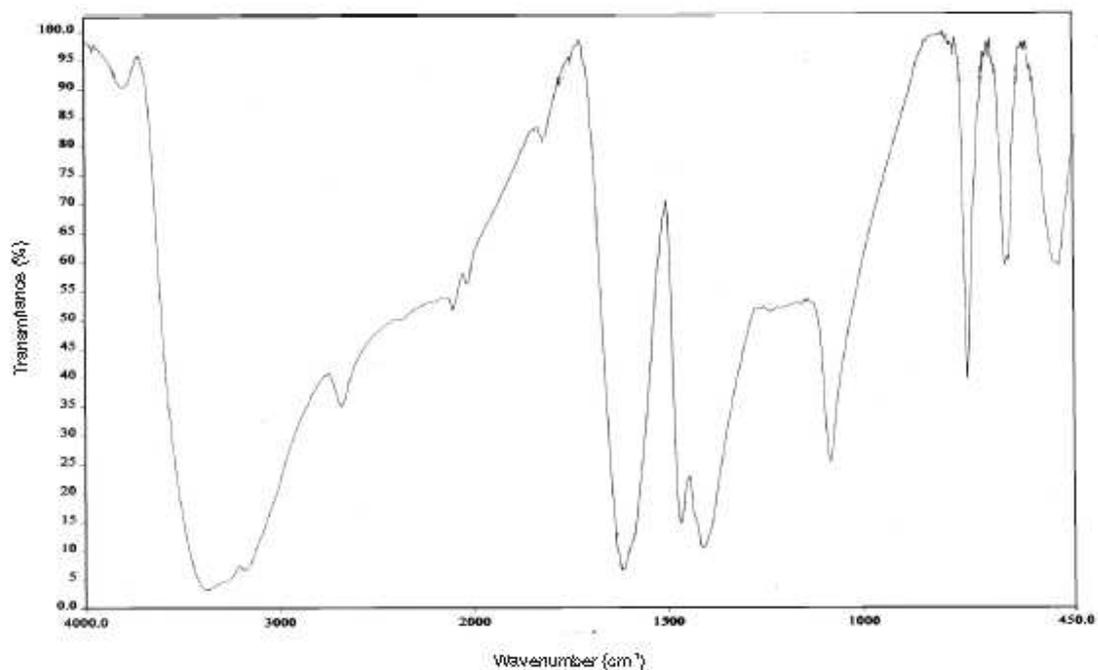
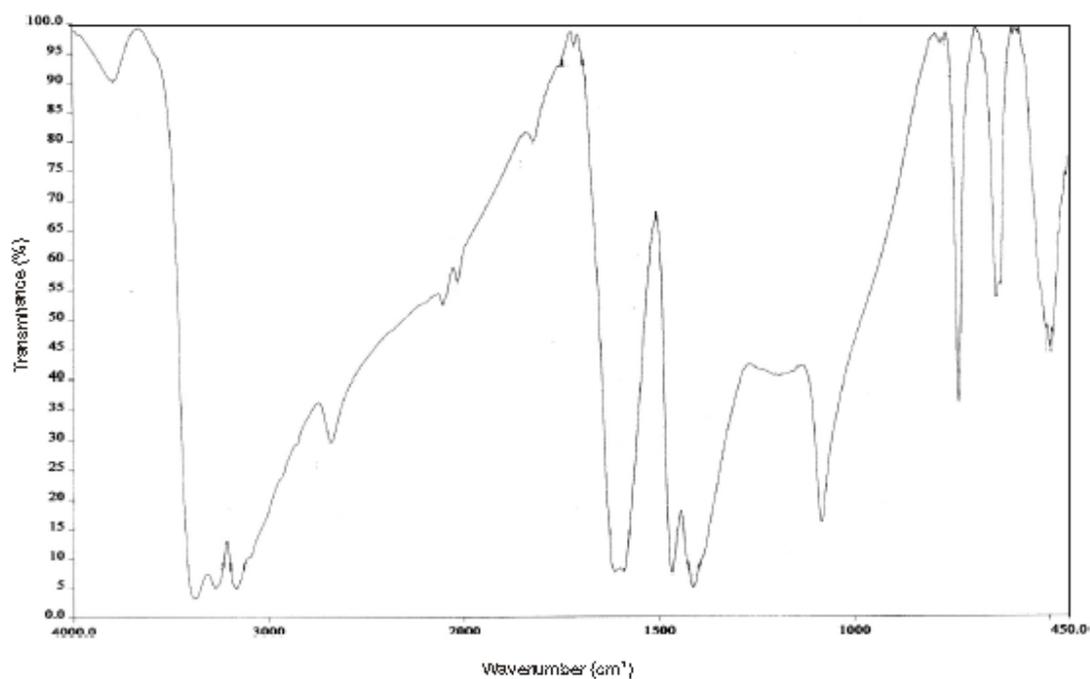**Fig.3.1   The FTIR spectra of pure BTMC crystal**

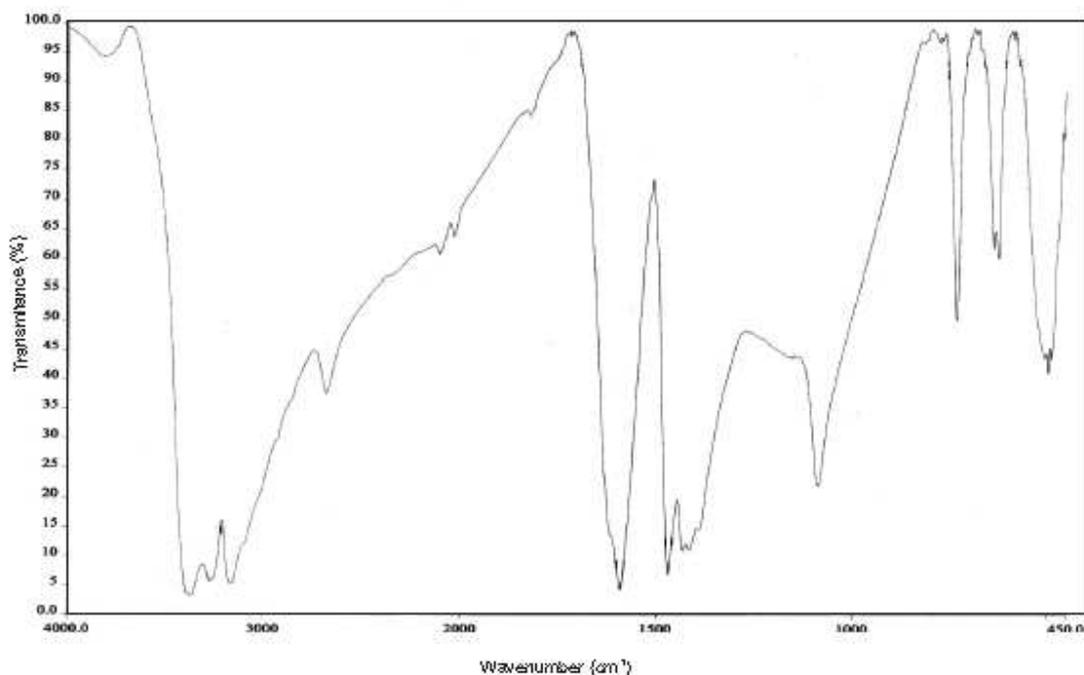**Fig. 3.2   The FTIR spectra of Cd²⁺ doped BTMC crystal**

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Fig. 3.3   **The FTIR spectra of Zn^{2+} doped BTMC crystal**

3.5 NLO TEST – KURTZ POWDER SHG METHOD

Growth of large single crystal is a slow and difficult process. Hence, it is highly desirable to have some technique of screening crystal structures to determine whether they are noncentrosymmetric and it is also equally important to know whether they are better than those currently known. Such a preliminary test should enable us to carry out the activity without requiring oriented samples. Kurtz and Perry [13] proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz [14] surveyed a very large number of compounds.

The SHG in the pure, Cd^{2+} and Zn^{2+} doped BTMC is confirmed by emission of green radiation from the respective samples. KDP crystal is taken as the reference material and the conversion efficiency of pure and doped BTMC crystals is studied. The results indicate that the efficiency of frequency doubling in Cd^{2+} doped (42 %) and Zn^{2+} doped (55 %) BTMC crystals are more than the pure BTMC (40 %) and the KDP (21%) crystals.

CONCLUSION

Single crystals of pure and metal doped BTMC are conveniently grown by employing slow evaporation technique. The XRD studies confirm the structure of grown crystals. The presence of dopants has marginally altered the lattice parameters without affecting the basic structure of crystals. The percentage of dopants present in the crystal lattice was determined by AAS. The optical absorption spectral studies confirmed that the crystals have low absorption with lower UV cut-off wavelength around 245 nm, which is an essential consideration for the NLO crystals. The FTIR studies revealed the shifting of CS stretching (1412 cm^{-1}) of thiourea to lower values and thereby ascertains the coordination of sulphur with metals. SHG of these crystals has been confirmed by NLO test. Hence, it can be concluded that the metallic dopants play a key role in improving the optical quality of the BTMC crystals.

REFERENCES

[1] Samyn Celest, Varbiest Thierry, Persoons Andre, Macromol Rapid communication **2000**, 21 (1): 1-15.
[2] Singer K. D, Sohn J. E., Appl. Phys. Lett., **1986**,49 (5): 248-50
[3] Chen M, Dalton L. R. Yu L.P, Shi Y. Q, Steier W.H. Macromolecules **1992**, 25 (15): 4032-35.

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[4] Jonsson J, Paulsson G, Samuelson L, J Appl. Phys. **1991**, 70(3): 1737-41.

[5] Ushashree P.M, Jayavel R, Subramanian C, Ramasamy P, J. Cryst. Growth, **1999**, 197, 216.

[6] Rajasekaran R, Ushashree P.M, Jayavel R, Ramasamy P, J. Cryst. Growth, **2000**, 218, 365.

[7] Rajasekaran R., Ushasree P.M, Jayavel R. and Ramasamy P. (**2001**), J. Crystal Growth, Vol. 229, pp. 563–567.

[8] Rajesh N.P., Kannan V., Ashok M., Sivaji K., Santhana Raghavan P. and Ramasamy P. (**2004**), J. Crystal Growth, Vol. 262, pp.561–566.

[9] Warren L.F. (**1990**), Proceedings of the Fourth International SAMPE Electronics Conference, Ed. Allred R.E., Martinez R.J. and Wischmann W.D. (Society for the Advancement of Material and Process Engineeing,Covina,Ca.,**1990**),Vol.4, pp.388-396.

[10]Albert Cotton F. and Wilkinson G. (**1970**), 'Advanced Inorganic Chemistry', second Ed., Wiley Eastern limited, New Delhi.

[11]Swaminathan K, Irving, H.M.N.H, J Inorg. Nucl. Chem. **1964**, (26) 1299.

[12]Nakamoto K. (**1978**), 'IR and Raman spectra of inorganic and coordination compounds', Wiley Inter.Science, New York.

[13]Kurtz S.K. and Perry T.T. (**1968**), J. Appl. Phys., Vol. 39, pp. 3798−38l3.

[14]Kurtz S.K (**1968**), 'New nonlinear optical materials', IEEE, J. Quantum Electron, Vol. 4, pp. 578-584.