

Synthesis, Crystal growth and Characterization of bis 2 - methyl thio imidazolium Copper Chloride dihydrate: A novel metal organic single crystal

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ABSTRACT

Single crystals of 2 – methyl thio imidazolium copper chloride dihydrate (BMTCC) with dimension $5 \times 5 \times 4 \text{ mm}^3$ were grown from slow evaporation technique at room temperature. The crystal structures of the grown crystal have been studied by single crystal X – ray diffraction analysis. The as grown crystal is in monoclinic system with space group P^{-1} . The grown crystal was subjected to powder X – ray diffraction studies to confirm crystallinity of the grown crystal. Functional groups of the crystallized molecules were confirmed by FT – IR spectroscopic analysis. Optical transparency range of the grown crystal was determined by UV – Vis – NIR spectroscopy. The lower optical cut off wavelength for this crystal is observed at 371 nm. Vickers microhardness test was performed on the well grown crystal surface of the grown crystal. The thermal behaviour of the grown crystal was determined with the aid of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The photoluminescence spectrum of the grown crystal was recorded and its optical band gap is about 1.6 eV.

Keywords: Growth from solution, X – ray diffraction, FT – IR spectroscopy, Optical properties, Thermal analysis.

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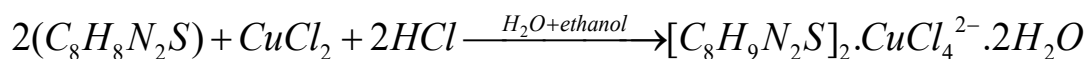
1.Introduction

Organic – inorganic hybrid materials have received increasing attention in recent research because of their ability to combine the specific properties of inorganic frameworks and the features of organic molecules [1 – 4]. Inorganic materials offer the potential for a wide range of electronic properties, magnetic and dielectric transitions, substantial mechanical hardness and thermal stability [5, 6]. Organic molecules, on the other hand can provide high fluorescence efficiency, large polarizability [7], plastic mechanical properties, ease of processing and structural diversity [8, 9]. Metal complexes of polarizable organic ligands are currently being explored for their optical properties. These have been commonly referred as organometallics, as their physical and chemical properties set them apart from usual organic and inorganics. Organometallics share advantages of both inorganics and organics, which include extended transparency, amenable crystal growth, good mechanical hardness and chemical inertness. Another remarkable advantage of this class is the

high resistance to laser induced damage. Single crystal of organic materials in practical application has been impeded by the inadequate transparency, poor optical quality and low laser damage threshold. The inorganic crystals have excellent mechanical and thermal properties, but they possess relatively modest nonlinearity because of lack of extended π electron delocalization [10]. The crystal structure of imidazolium sulphate dihydrate was reported by Freeman et al. [11]. Fukunaga and Ishida have been reported on the crystal structure of imidazolium hydrogen tartrate [12]. The crystal structure of Bis (imidazolium) hexachloro stannate (IV) and bis (imidazolium) tetrachlorocobaltate (II) was reported earlier on literature [13, 14]. Phosphoric acid imidazolium dihydrogen phosphate crystal structure was reported by Chen et al. [15]. Bis imidazolium galactarate dihydrate have been reported by Smith and Wermuth [16].

In the present investigation 2 – methyl thio imidazolium copper chloride dihydrate (BMTCC), a

desirable organometallic single crystal was grown from aqueous solution using slow evaporation technique. The grown crystal was subjected to various characterization techniques such as single crystal and powder XRD, Fourier transform infrared analysis, UV – Vis – NIR, mechanical hardness study, thermal analysis, photoluminescence and scanning electron microscopy analysis were discussed in detail. The grown crystal structure, growth and characterizations of BMTCC are reported for the first time in the literature.



The prepared solution was stirred well and the resultant BMTCC was formed by mixing the starting materials. This solution was heated and kept for slow evaporation to dryness at room temperature. The purity of the synthesized salt was improved by a successive recrystallization process.

2.2 Crystal growth

Optically good quality crystals of BMTCC were grown from aqueous solution by slow evaporation technique at

2. Experimental Procedure

2.1 Materials synthesis

The BMTCC salt was synthesized by high purity 2 methyl thio imidazolium and copper chloride in a stoichiometric ratio of 2:1. The calculated amount of starting materials was dissolved in double distilled water and ethanol at room temperature. The precursor compound was prepared according to the reaction

room temperature. The synthesized salt of BMTCC was used to grow single crystal. The saturated solution was prepared and then filtered to remove any insoluble impurities. The filtered solution was transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation technique at room temperature. Well defined, transparent crystals of good quality were obtained. BMTCC single crystals of dimension up to $5 \times 5 \times 4 \text{ mm}^3$ were grown over a period of 10 days. As grown single crystals of BMTCC is shown in Fig. 1.



Fig. 1 As grown single crystal of BMTCC

3. Results and discussion

3.1 Single crystal X – ray diffraction

The unit cell parameters and the crystal structure were determined from single crystal X – ray diffraction data obtained with a three circle Bruker platform diffractometer (graphite monochromator) with Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure was solved by direct methods and full matrix least squares refinements were performed on F²

using all unique reflections. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms were refined with isotropic displacement factors. Drawings of the molecular structure and the packing diagram of the grown crystal are shown in Fig. 2 and Fig. 3. Further crystal data, experimental conditions and structural refinement parameters are presented in Table 1.

Table 1 Crystal data and structure refinement for BMTCC

Formula	C ₁₆ H ₂₂ Cl ₄ CuN ₄ O ₂ S ₂
Formula weight	571.86
Crystal color, habit	Block, Orange, plate
Crystal system	Monoclinic
Crystal size	0.3 × 0.2 × 0.2 mm ³
Space group	P ⁻¹
Z	2
Unit cell dimensions	a = 8.059 (2) Å α = 81.441 (10)° b = 8.387 (2) Å β = 81.490 (10)° c = 18.814 (5) Å γ = 73.223 (10)°
Volume	1196.54 Å ³
Diffractometer	Bruker SMART APEX CCD
Radiation	Mo Kα
Wavelength	0.71073 Å
Temperature	293 K
Refinement method	Full – matrix least square on F ²
Absorption correction	Multi – scan (<i>SADABS</i> , Bruker, 2004)

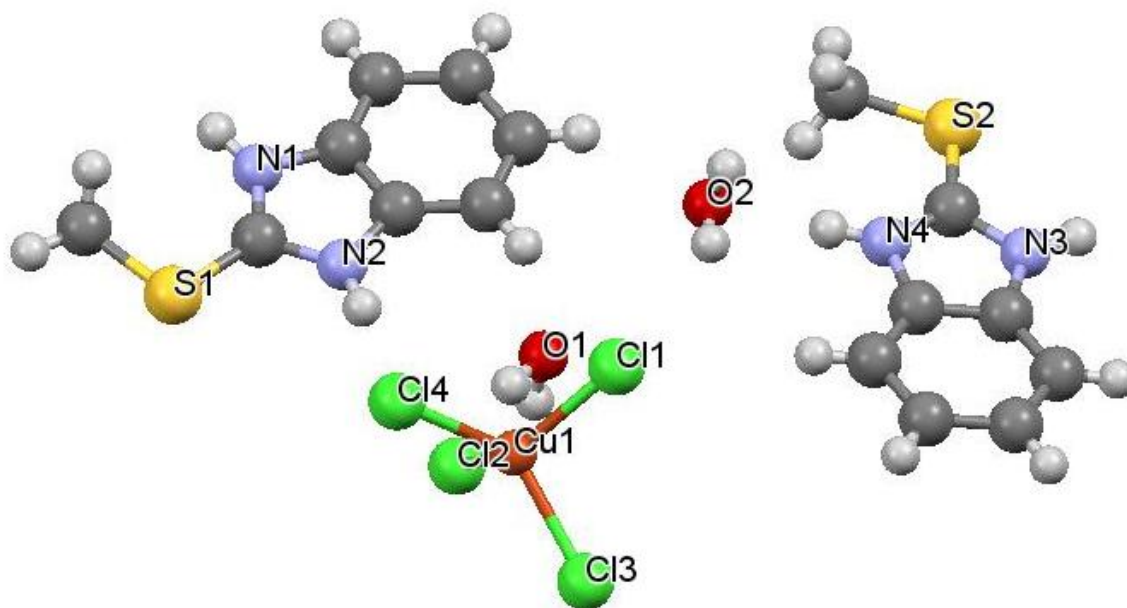


Fig. 2 Crystal structure of BMTCC single crystal

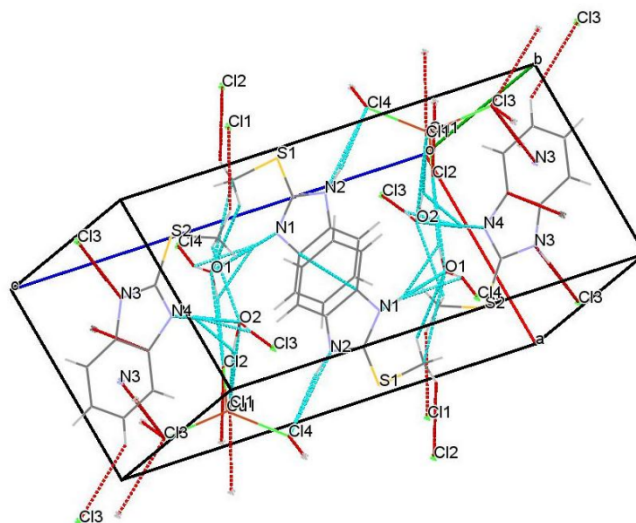


Fig. 3 Packing diagram of BMTCC illustrating with hydrogen bonding scheme

3.2 Powder X – ray diffraction analysis

The crystalline nature of the grown crystal was checked by taking the X – ray diffraction pattern of the powdered samples using BRUKER X – ray diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The grown crystal was scanned in the range of $10 - 80^\circ$ at the scanning rate of $2^\circ/\text{min}$.

The obtained 2 θ values are indexed using AUTOX – 93 software package. The indexed powder XRD pattern is shown in Fig. 4. The presences of sharp peaks are indicating the good crystalline nature of the grown BMTCC single crystal.

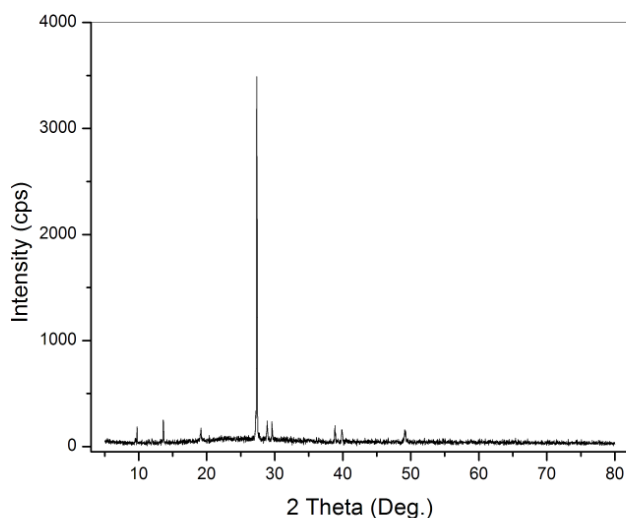


Fig. 4 Powder X – ray diffraction pattern of BMTCC

3.3 Fourier transforms infrared spectroscopy

The presence of various functional groups in the BMTCC crystal was confirmed from the FTIR spectral analysis. The FTIR spectrum was recorded using Perkin Elmer FTIR spectrometer in the mid IR region of $400 - 4000 \text{ cm}^{-1}$. The recorded FTIR spectrum is shown in Fig. 5. The tentative

vibrational band assignment [17, 18] for BMTCC crystal is given in Table 2. The peaks at 3216 and 3060 cm^{-1} are assigned to O – H stretching vibrations respectively. The band at 2943 and 2840 cm^{-1} established the presence of NH asymmetric and symmetric stretching vibrations respectively. The peak at 1641 cm^{-1} is due to the presence

of NH₂ deformation. The C – N – H stretching vibration observed at 1542 cm⁻¹.

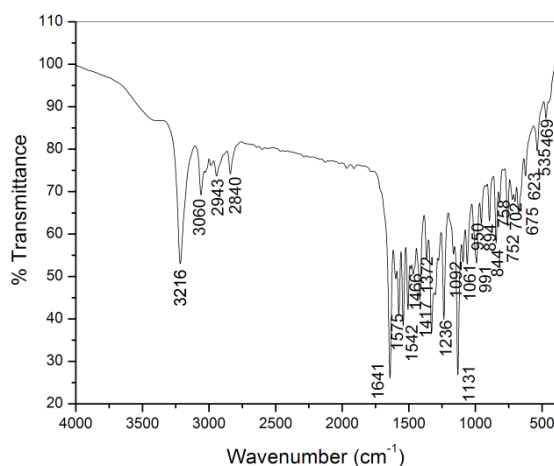


Fig. 5 FT - IR spectrum of BMTCC single crystal

The band at 1466 and 1417 cm⁻¹ signifies the presence of CH₂ bending and C = C stretching vibrations respectively. The presence of C – C – H bending vibration is clearly illustrated by the peak at 950 cm⁻¹. The stretching vibration of C – C – N is observed at 894 cm⁻¹. The CH₂ rocking and OH₂ bending vibrations are shown by the characteristic vibrations at 844 and 702 cm⁻¹.

Table 2 Tentative band assignments for BMTCC single crystals

Wavenumber (cm ⁻¹)	FT - IR band assignments
3216	O – H asymmetric stretching vibration
3060	O – H symmetric stretching vibration
2943	N – H asymmetric stretching vibration
2840	N – H symmetric stretching vibration
1641	NH ₂ deformation vibration
1542	C – N – H stretching vibration
1466	CH ₂ bending vibration
1417	C = C stretching vibration
1372	CH ₂ Wagging vibration
1236	C – N stretching vibration
1131	N – H bending vibration
1092	C – H bending vibration
1061	C – H bending vibration
991	C – C – N bending vibration
950	C – C – H stretching vibration
894	C – C – N stretching vibration
844	CH ₂ rocking vibration

758	OH bending vibration
752	C – C bending vibration
702	OH ₂ bending vibration
675	NH wagging vibration
623	CH ₂ scissoring vibration
535	CH wagging vibration
469	H – O – H wagging vibration

3.4 UV – Vis – NIR spectroscopic

The UV – Vis – NIR spectrum gives information about the structure of the molecule since the absorption of UV and visible light involves the promotion of electron in σ and π orbitals from the ground state to higher energy states [19]. The UV – Vis – NIR transmittance spectrum of BMTCC

crystal was recorded between the wavelength ranges of 190 – 1000 nm using Perkin Elmer Lambda 35 UV – Vis – NIR spectrophotometer. The recorded spectrum of BMTCC crystal is shown in Fig. 6. The ultra violet transmission spectrum is very important for any optical material because of its wide transmittance window.

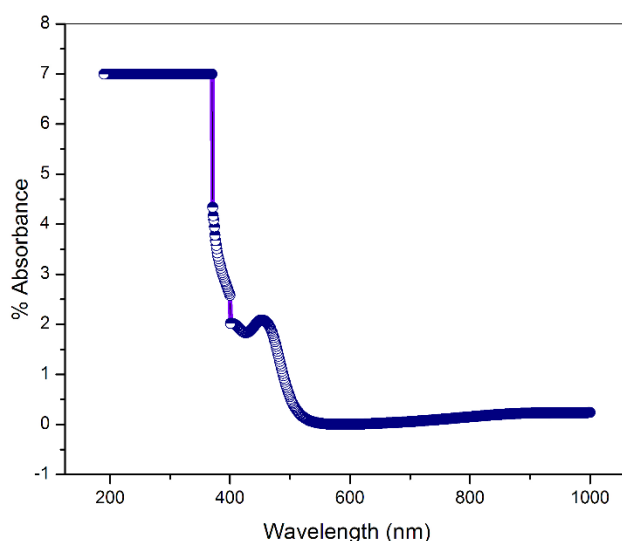


Fig. 6 UV – Vis – NIR absorbance spectrum of BMTCC

The cut off wavelength as observed from the absorbance spectrum is 371 nm, which is sufficient for SHG laser radiation. Interestingly, in the entire visible region starting from 550 to 1000 nm, the crystal has almost no absorption. The wide optical transmission window is an encouraging optical property seen in BMTCC crystal and is of vital important role for NLO materials.

3.5 Microhardness studies

Hardness is one of the important mechanical properties of the materials. They can be used as a suitable method for measure the strength of the materials. Microhardness measurements were carried out using Vickers microhardness tester fitted with a diamond pyramidal

indenter. The good quality grown single crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitudes were applied over affixed interval of time. The indentation time was kept at 10 s for all trials. The Vickers microhardness number was calculated using the relation $H_v = 1.8544 (P/d^2)$ kg/mm², where P is the applied load in kg and d is the diagonal length of the indentation impression in mm. The graph was drawn between the hardness numbers and applied load and is shown in Fig. 7. The hardness value increases gradually with the increase of load and above 100 g cracks developed on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. The increase in the microhardness values of BMTCC with

increasing load is in agreement with the reverse indentation size effect (RISE). The plot of $\log d$ versus $\log P$ is shown in Fig. 8 and it gives a straight line. According to Meyers power law $P =$ and, where n is the work hardening coefficient or Meyers index number. From careful observations on various materials, Onitsch [20] and Hanneman [21] pointed out that n lies between 1 and 1.6

for moderately hard materials and it are more than 1.6 for soft materials. The value of n for BMTCC crystal is calculated as 2.6, which confirms that the crystal belongs to soft material category. The slope of 2.6 reveals that the material has a moderate hardness coefficient and it is useful for device applications.

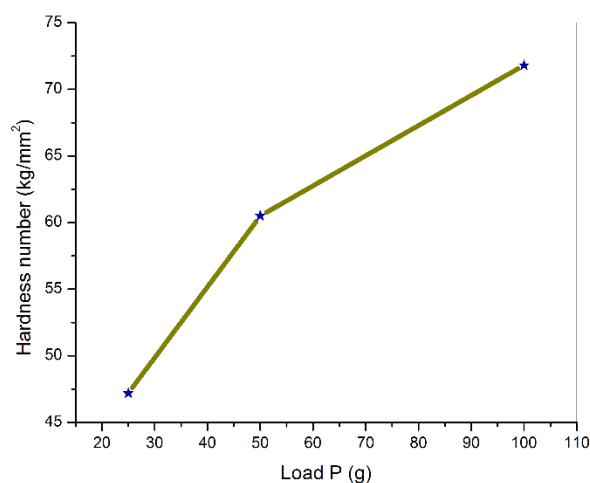


Fig. 7 Hardness behaviour of BMTCC single crystal

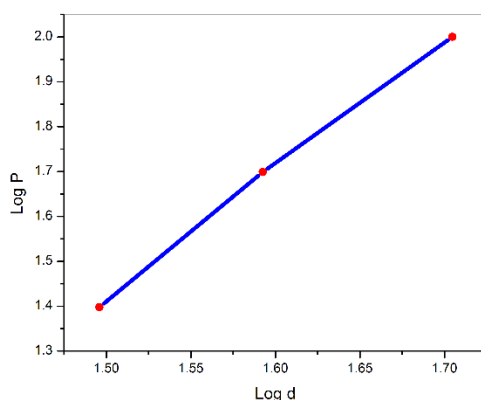


Fig. 8 Meyers plot ($\log d$ vs. $\log P$) of BMTCC single crystal

3.6 Thermal analysis

The thermogravimetric (TG) and differential thermal analyses (DTA) of the grown crystal was carried out for the sample weight of 4.499 mg from the temperature 25 – 850 °C in nitrogen gas atmosphere at a heating rate of 10 °C/min using SDT Q600 thermal analyzer. The recorded TG/DTA graph is shown in Fig. 9. From the figure, it is

observed that, the BMTCC molecules starts to melt around 54 °C. Hence, the material can be thermally stable up to 54 °C. When continuously heating the compound, the BMTCC crystal starts to decompose with three different stages of weight loss. During the first stage of weight loss, there is a loss of 5.3 % was observed, which may be due to the loss of two water molecules.

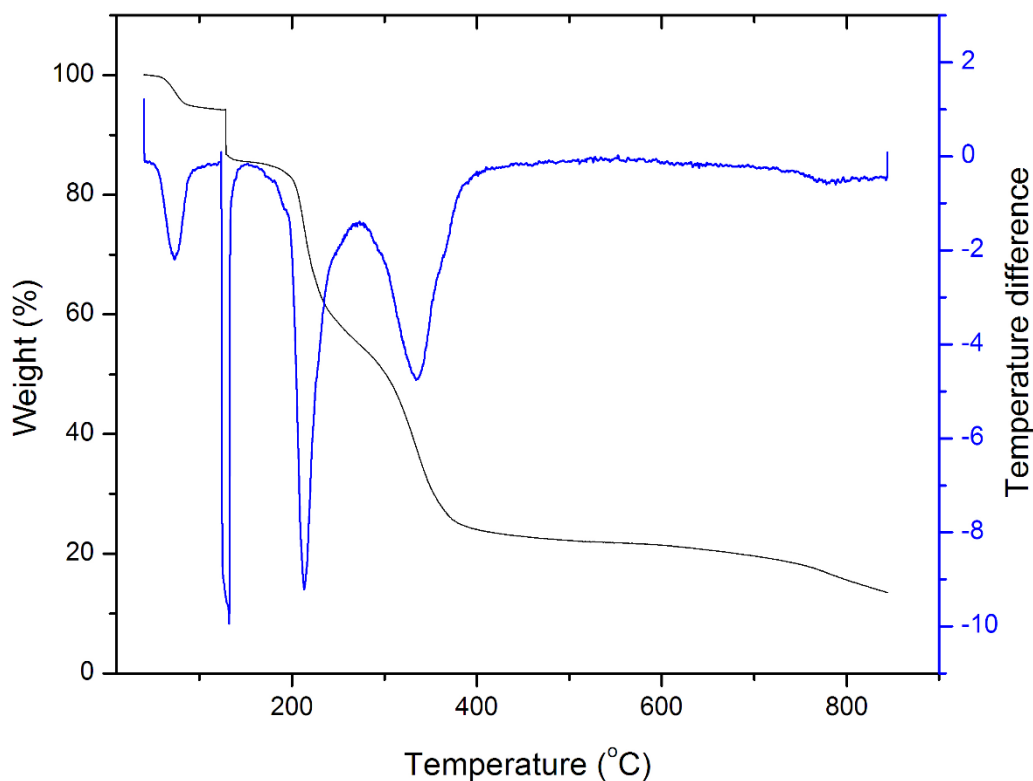


Fig. 9 TG/DTA graph for BMTCC single crystal

The second step of weight loss is observed between the temperature ranges of 128 – 233 °C. This step of weight loss is due to the loss of one 2 methyl thio imidazole molecule. In the last stage of decomposition a weight loss of 48 % was observed between 233 °C and 841 °C. Between these temperature regions, remaining one 2 methyl thio imidazole and copper tetrachloride molecules may be released. Based on the result of TGA analysis the maximum temperature for NLO application of this crystal is limited to 54 °C.

3.7 Photoluminescence analysis

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and excited energy is released as light. The photon energies reflect the variety of energy states that are present in the materials.

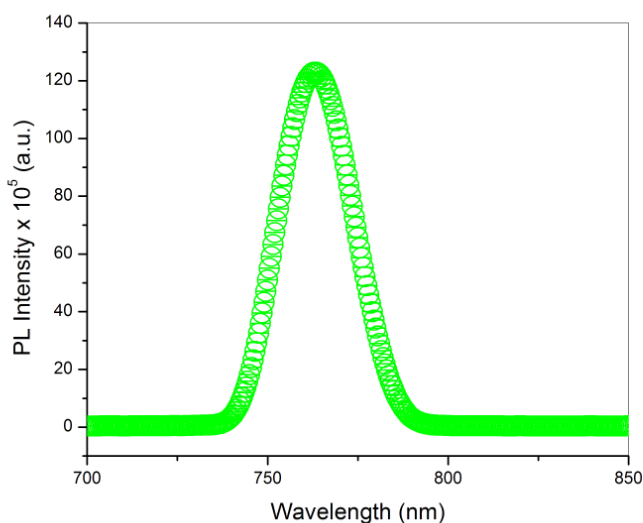


Fig. 10 Photoluminescence spectrum of BMTCC crystal

In the present study, luminescence behavior of BMTCC has been carried out using Ar⁺ ion laser operating at 488 nm and 5mW (corresponding to 0.125 Wcm⁻²) for excitation in all the measurements. The as grown inclusion free single crystal of BMTCC was scanned between 400 nm to 900 nm and the excitation wavelength is 360 nm. The graph was plotted against PL intensity Vs. wavelength is shown in Fig. 10 and found that the maximum PL intensity was appeared at 740 nm and 800 nm. The highest emission peak from the spectrum was observed to be at 760 nm. In the conversion from wavelength to energy, the energy band gap at this wavelength was calculated to be 1.6 eV using the formula $E_g = hc/\lambda$. Where h is the Planck's constant, c is the velocity of light and λ is the wavelength of luminescence.

3.8 Surface micro-morphology analysis

Morphology of as grown surfaces of bulk single crystals and epitaxial layers consists of variety of structures. The

shape of a growth spiral depends on the nature of growth parameters like supersaturation, temperature, impurities and mass and heat transport processes. In the present study, the surface micro morphological analysis has been carried out on the well-grown single crystal of BMTCC using Jeol Stereo scan microscope. Since organic is non-conducting in nature, so the smooth surface of the specimen is coated with carbon. Fig. 11 and Fig. 12 depict the different magnification surfaces of as grown BMTCC single crystal. From the figure it is observed that the screw type growth mechanism [22] has been identified from the bottom of the specimen (Fig. 11). This is because of the bottom surface may not get the sufficient saturated solution, which is the mandatory requirement for good crystal growth. This causes the spiral pattern in the bottom of the specimen. Where as in the surface of the specimen (Fig. 12) shows the line type defects are quite commonly observed in solution grown crystals, which is mainly due to the capture of dislocations or impurities during growth.

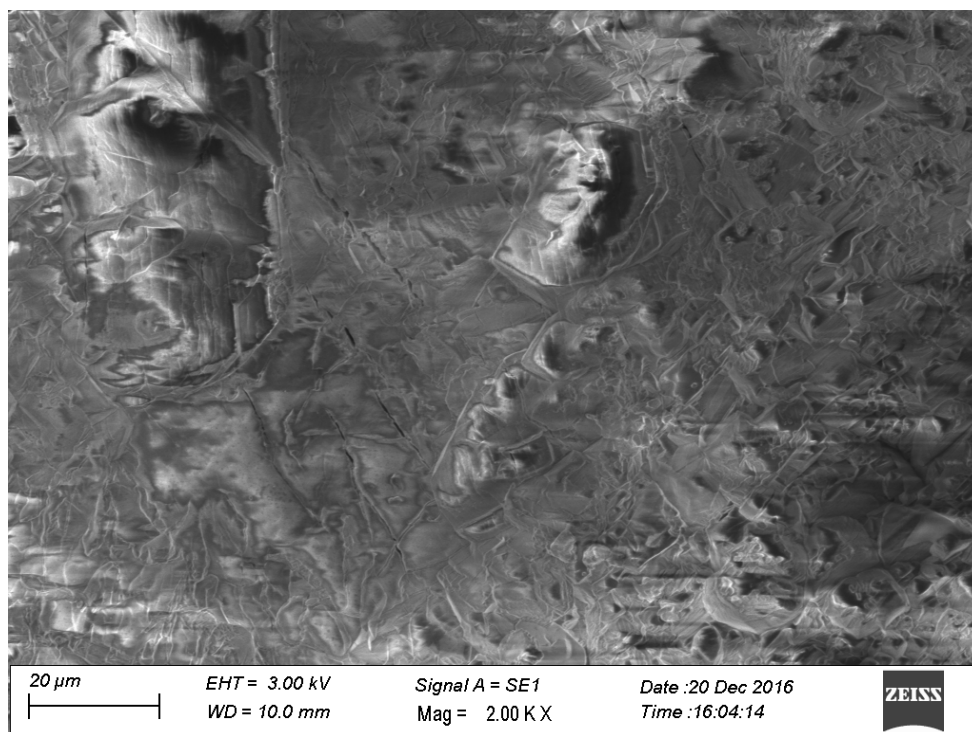


Fig. 11 SEM photographs of as grown BMTCC for magnification at 2 kx

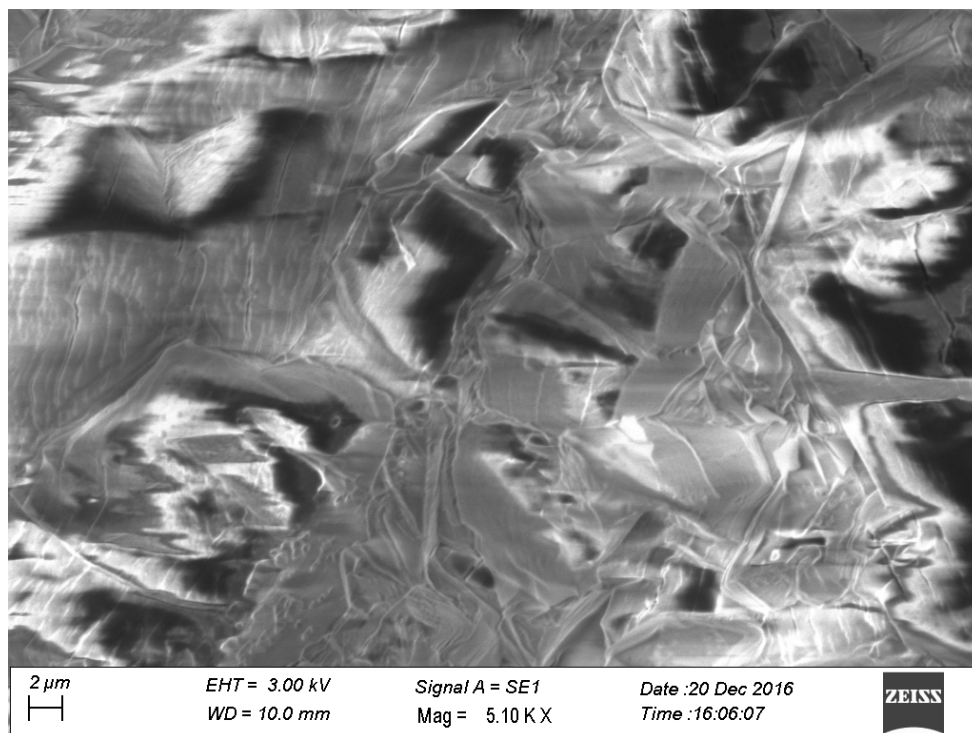


Fig. 12 SEM photographs of as grown BMTCC for magnification at 5.10 kx

4. Conclusion

Bulk single crystals of BMTCC were successfully grown from slow evaporation technique at room temperature. Single crystal X – ray diffraction analysis was carried out

to calculate the lattice parameters and solve the crystal structure of the grown BMTCC single crystal. The grown crystal belongs to the monoclinic system with space group $P-1$. The crystalline nature of the grown BMTCC single

crystal was confirmed by powder X – ray diffraction analysis. Various functional groups present in the grown crystal were identified by FT – IR spectral analysis. BMTCC single crystals were optically transparent in the entire visible region with a lower cut off wavelength 371 nm. The good transmission property of the BMTCC crystal in the entire visible region ensures its suitability for SHG applications. The hardness studies showed the increasing nature of hardness number with increase in applied load. The mechanical stability of BMTCC crystal was found to be 100g. The thermogravimetric analysis revealed that the material was thermally stable up to 54 °C. Thus, the BMTCC acted as a good crystal and it had a number of novel applications in optoelectronic devices.

REFERENCES

1. P. J. Lindner, E. Bender, R. S. Besser, Failure analysis of novel microhollow cathode discharge microplasma reactors, *Int. J. Hydrogen Energy* 36 (2014) 2898
2. E. Bernordo, L. Fiocco, G. A. Giffin, V. Di Noto, P. Colombo, Microstructure Development and Dielectric Characterization of Forsterite-Based Ceramics from Silicone Resins and Oxide Fillers, *Adv. Eng. Mater.* 16 (2014) 806
3. S. Kitajima, F. Bertasi, K. Vezzu, E. Negro, Y. Tominaga, V. Di Noto, Dielectric relaxations and conduction mechanisms in polyether–clay composite polymer electrolytes under high carbon dioxide pressure, *Phys. Chem. Chem. Phys.* 15 (2013) 16626 – 16633.
4. G. A. Giffin, G. M. Haugen, S. J. Hamrock, V. Di Noto, Interplay between Structure and Relaxations in Perfluorosulfonic Acid Proton Conducting Membranes, *J. Am. Chem. Soc.*, 135 (2013) 822 – 834.
5. F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, All-polymer field-effect transistor realized by printing techniques, *Science* 265 (1994) 1684 – 1686
6. S. F. Nelson, Y. Y. Lin, D. J. Gundlach, T. N. Jackson, Temperature-independent transport in high-mobility pentacene transistors, *Appl. Phys. Lett.* 72 (1998) 1854 – 1856
7. P. Szklarz, R. Jakubas, G. Bator, T. Lis, V. Kinzhybalov, J. Baran, Structural characterization, spectroscopic properties and phase transition in 4-aminopyridinium tetrachlorogallate(III): [4-NH₂PyH] [GaCl₄], *J. Phys. Chem. Solid* 68 (2007) 2303 – 2316
8. D. B. Mitzi, K. Chondroudis, C. R. Kagan, *Organic-inorganic electronics*, IBM. J. Res. Dev. 45 (2001) 29 – 45
9. I. Cheabane, F. Hlel, K. Guidara, Electrical study by impedance spectroscopy of the new compound [C₁₂H₁₇N₂]₂CdCl₄, *J. Alloys Compd.* 461 (2008) 495 – 500
10. H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunningham, C.A. Thomas, L.A. Deloach, S.P. Velsko, C.A. Ebberts, J.H. Liao, M.G. Kanatzidis, 1-Histidine tetrafluoroborate: a solution-grown semiorganic crystal for nonlinear frequency conversion, *Opt. Lett.* 20 (1995) 252 – 254.
11. H.C. Freeman, F. Huq, J.M. Rosalky and I.F. Taylor Jr, The crystal and molecular structure of imidazolium sulphate dihydrate, *Acta Cryst.* B31 (1975) 2833 – 2837.
12. T. Fukunaga and H. Ishida, Imidazolium hydrogen tartrate, *Acta Cryst.* E59 (2003) o1869 – o1871
13. H. Zhang, L. Fang, R. Dronskowsk, K. Kruse and R. Yuan, Bis(imidazolium) hexachlorostannate, *Acta Cryst.* E61 (2005) m543 – m544
14. H. Zhang, L. Fang and R. Yuan, Bis (Imidazolium) tetrachlorocobaltate, *Acta Cryst.* E61 (2005) m677 – m678
15. C. Chen, P. Y. Zavalij and M.S. Whittingham, phosphoric acid imidazolium dihydrogen phosphate, *Acta Cryst.* E62 (2006) o258 – o260
16. G. Smith and U. D. Wermuth, Bis (imidazolium) galactarate dihydrate, *Acta Cryst.* E66 (2010) o2399
17. K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination compounds*,
18. Wiley, New York, 1978
19. George Socrates, *Infrared and Raman characteristic group frequencies*, John Wiley, New
20. York, 2001
21. B. K. Periyasamy, R. S. Jebas, B. Thailampillai, Synthesis and spectral studies of 2-aminopyridinium para-nitrobenzoate: A novel optoelectronic crystal, *Mater. Lett.* 61 (2007) 1489 – 1491.
22. E. M. Onitsch, *Mikroskopie* 2 (1947) 131
23. Hanneman, M. *Metall.* 23 (1941) 135
24. K. Sangwal, R. Rodriguez-Clemente, *Surface morphology of crystalline materials*, Trans
25. Tech Publications, USA, 1991