

Focusing Photoluminescence Properties of Bis Thiourea Cadmium Acetate Crystal Exploiting Organic Ligand of Oxalic Acid for NLO Device Applications

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Abstract: *Modifying optical properties of crystal is very fundamental need for designing various photonic devices hence in current investigation the oxalic acid (OA) has been firstly doped in Bis thiourea cadmium acetate (BTCA) crystal with aim to optimize the luminescence properties of BTCA crystal. The crystals have been grown by slow solvent evaporation technique at 35°C. The structural parameters of grown crystals have been determined using the single crystal X - ray diffraction technique. The incorporation of OA in BTCA crystal matrix has been confirmed by Fourier transform infrared analysis. The color centered luminescence studies have been carried out which established the prominent red shift in peak maxima of emission wavelength of BTCA crystal due to doping of OA.*

Keywords: Crystal growth, single crystal X - ray diffraction technique, luminescence

1. Introduction

Thiourea metal coordinated complex crystals have stretched the attention in last few decades due to their unique credibility of beholding the properties semiorganic counterparts. Hence such crystals are ranked as superior materials for designing advance nonlinear optical (NLO) devices [1 - 4]. The umbrella of thiourea metal complex crystals is quite big amongst which some of the promising semi organic crystals are under constant investigation [5 - 7]. The transition element materials possessing closed d^{10} shell electrons express superior optical properties [8], So BTCA is the interesting beneficial material to investigate for finding its applicability for suitable nonlinear optical device applications. The intruding fact from literature survey is that very few research groups have explored the characteristic features of pure BTCA crystal [9 - 11]. Hence published there are very few reports on doping of impurity in BTCA crystal. The modification in the intrinsic and extrinsic properties of host crystal is effectively possible through doping [12], the impact of amino acid doping viz. glycine, L - alanine, L - cysteine and L - valine on distinct properties of BTCA crystal has been explored [13 - 15]. Review of various path breaking reports claimed that the organic dopants having the donor - π - acceptor moieties and better polarizing behaviour reinforce the constructive impact on optical properties of parent crystal [16 - 17].

As OA (oxalic acid) is known to have abundance of π - bonded network that is the foremost requirement for

enhancing the NLO properties and the electronic response time of crystals [16]. So, OA proves its suitability as a dopant for optimizing the optical modifications in BTCA crystal. Under this current research investigation the significant effect of OA on structural and photoluminescence properties of BTCA crystal has been studied first time. The investigation has been accomplished by employing the single crystal X - ray diffraction, Fourier Transform Infrared spectroscopy and photoluminescence characterization techniques.

2. Experimental Procedure

BTCA metal complex salt has been synthesized by dissolving cadmium acetate (1mole) and thiourea (2mole) in de - ionized doubly distilled water. Purity of BTCA has been obtained by the repetitive re - crystallization process. Oxalic acid in 0.5M% was doped in the supersaturated solution of purified BTCA. These solutions were allowed to agitate for ten hours to achieve homogeneous mixing of dopant and host material. The homogeneously doped BTCA solution was filtered in the separate beaker using the standard Whatman No.1 filter paper and kept for slow solvent evaporation process in a constant temperature bath at 35°C ($\pm 0.01^\circ\text{C}$). Optically good quality crystals of OA - BTCA and were grown by spontaneous nucleation process after twenty days. The grown BTCA & OA - BTCA crystals are shown in Fig.1.

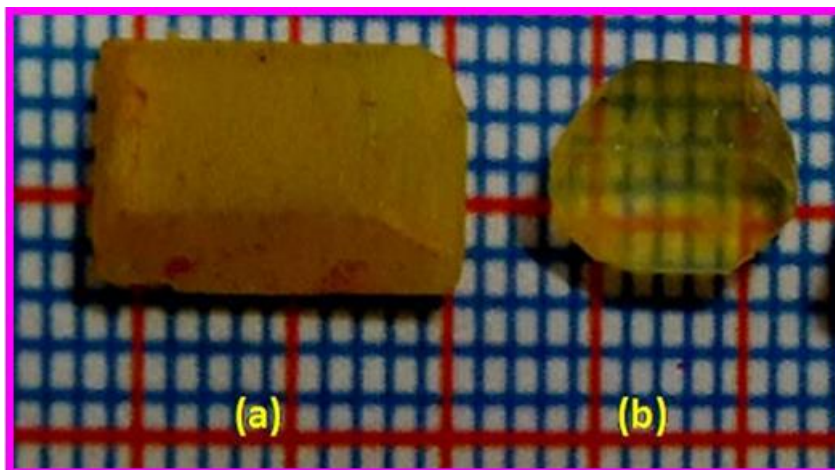


Figure 1: (a) Parent BTCA (b) OA - BTCA

3. Results and Discussion

3.1 Single crystal X – ray diffraction (XRD) analysis

The single crystal XRD technique was employed using the Enraf Nonius CAD4 X - ray diffractometer to determine the structural parameters of grown parent BTCA and OA - BTCA crystals. The XRD data shown in **Table 1** was

Table 1: Single crystal XRD data

Crystal	a (Å)	b (Å)	c (Å)	Volume (Å) ³	Crystal system
BTCA	7.57	11.79	15.41	1374	Orthorhombic [20]
OA - BTCA	7.571	11.807	15.424	1379	Orthorhombic

3.1 Fourier transform infrared analysis

The qualitative analysis of parent and doped crystals has been performed by means of FT - IR spectral analysis using the Bruker α - ATR spectrophotometer. The FT - IR spectrum of parent BTCA, and OA - BTCA was recorded in the range of 600 - 4000 cm^{-1} and is plotted in **Fig.2 (a), and (b)**. The C - N deformation is observed at 621, 660 and 654 cm^{-1} . The C - S stretching vibration associated with thiourea of BTCA is evident at 890, 812 and 832 cm^{-1} . The C - H deformation occurred at 992, 991 and 933 cm^{-1} . The CH_2 wagging is evident at 1397, 1394 and 1397 cm^{-1} . The C - O - O stretching is observed at 1481, 1465 and 1464 cm^{-1} . The peaks of NO_2 antisymmetric stretching in grown crystals is contributed at 1549, 1546 and 1549 cm^{-1} . The evidence of C=O bond stretching of carboxyl group is found at 1760 cm^{-1} . The characteristic C - C stretching vibrations are attributed at 2351, 2350 and 2368 cm^{-1} . The NH_2 stretching is assigned at wavenumber 3263, 3315 and 3297 cm^{-1} . The peaks contributed with 3300 - 4000 cm^{-1} are contributed by NH and OH bond stretching vibrations. The vibration peaks are indexed in FT - IR spectrum and the observed shift in wavenumber of identified functional groups are

recorded at room temperature and it confirmed the orthorhombic crystalline structure of Parent Crystal [20], OA - BTCA crystals. The analysis of XRD data evidences that the unit cell parameters of OA - BTCA crystal show slight variation with reference to Parent BTCA crystal [20], and the difference in cell volume infers the potential role of dopants OA in modifying the lattice dimensions of BTCA crystal.

distinguished in **Table 2**. The FTIR spectrum of parent BTCA and doped BTCA crystals is shown in **Fig.2 (a), and (b)** respectively. The identified shift in functional frequencies confirms the incorporation of dopants OA in BTCA crystal.

Table 2: FT - IR spectral assignments

Wavenumber (cm^{-1})		Functional group assignment
BTCA	OA - BTCA	
621	660	C - N deformation
890	812	C=S stretching
992	991	C - H deformation
1136	1134	N - C - N stretching
1397	1394	C H_2 Wagging
1481	1465	C - O - O stretching
1549	1546	NO_2 antisymmetric stretching
1667	1626	NH_2 bending
1743	1760	C=O stretching
2351	2350	C - C stretching
3052	3137	N - H stretching
3263	3315	NH_2 stretching
3300 - 4000		NH and OH stretching

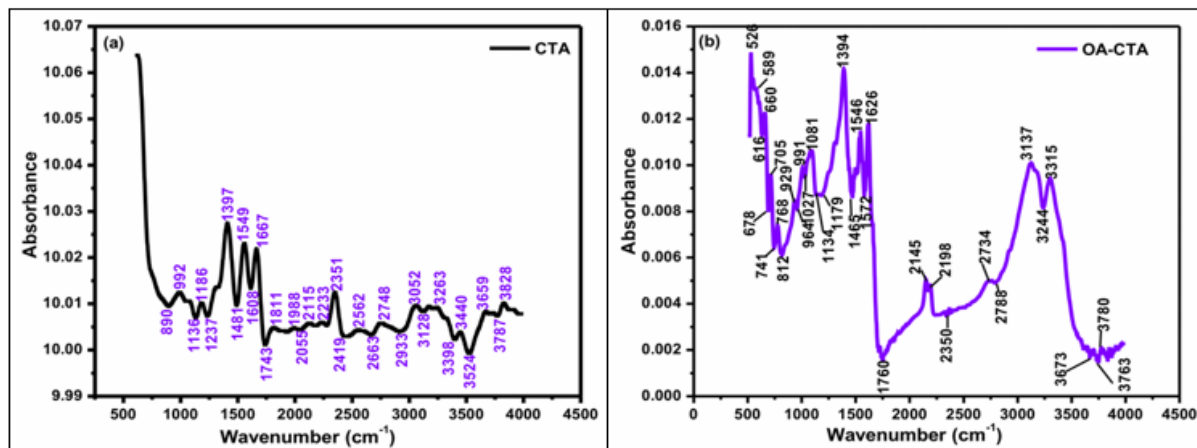


Figure 2: FTIR spectrum of (a) Parent BTCA (b) OA - BTCA

3.3 Photoluminescence Study

The color centered luminescence study gives the core understanding of energy states, trajectory of electron and electronic purity of the material [18 - 19]. The doping of specific impurity leads to defect formation which are optically active and this hampers the trajectory of electron during photo - relaxation giving rise to new/modifies luminescence properties. The respective materials were photo - excited at the energy wavelength of 354 nm and the photoluminescence (PL) emission spectrum was recorded in visible range of interest. The recorded PL spectrum of pure and doped BTCA crystal materials are shown in Fig.3.

The PL emission peak maxima was found to be at 481 nm (BTCA) [20] and 498 nm (OA doped BTCA) which confirms that the dopant reinforces the red shift in peak maxima of PL emission of BTCA crystal material. The modified PL emission of doped BTCA crystal thus confirms that the photo - excitation of material at specific energy governs the effective interaction of dopant and host crystal matrix moieties resulting to successful tuning of PL properties of BTCA crystal. The materials with promising PL emission tendency seek huge demand for detection purpose in biomedical and biochemical systems [21 - 22] which advocates the potential applicability of doped BTCA crystals for discussed applications.

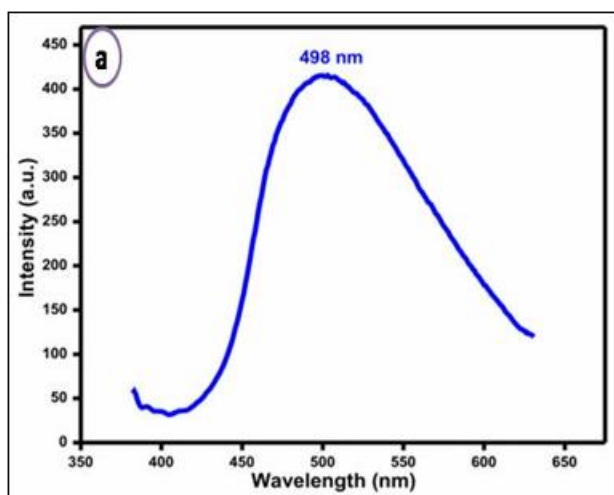


Figure 3: PL emission peak maxima of OA - BTCA

4. Conclusion

The parent and BTCA and OA doped BTCA single crystals have been successfully grown by slow solvent evaporation technique and characterized to explore the constructive impact of OA on structural and photoluminescence properties of BTCA crystal. The structural parameters of parent and doped BTCA crystals have been confirmed by Single Crystal XRD analysis. The identified functional groups in FTIR analysis confirmed the presence of OA in BTCA crystal. The PL studies revealed that the BTCA crystal has emission at 481 nm while the OA doped BTCA crystal has the maximum emission at 498 nm and 518 nm. The doping of OA facilitates the red shift in emission peak maxima of BTCA crystal. The comparative analysis thus confirms that the OA effectively tailors the studied optical properties of BTCA crystal which makes them the better alternative for designing distinct NLO device applications.

Acknowledgments

Authors are grateful to Dr. M. S. Pandian (S. S. N. College of Engineering, Chennai, India) for extending the photoluminescence facility.

References

- [1] Gary L. Succaw, Timothy J. R. Weakley, Fusan Han, Kenneth M. Doxsee, *Crystal Growth & Design* 5 (2005) 2288 - 2298. DOI: 10.1021/cg050162c
- [2] Ming Li, Mingjun Xia, Huining Xia, *Chemistry Select* 2 (2017) 5882 - 5886. DOI: 10.1002/slct.201701038
- [3] K. Ramamurthi, G. Madhurambal, B. Ravindran, M. Mariappan, S. C. Mojumdar, *J Thermal Calorim* 104 (2011) 943-947. DOI: 10.1007/s10973 - 011 - 1492 - y
- [4] S. M. Azhar, S. S. Hussaini, M. D. Shirsat, G. Rabbani, Mohd Shkir, S. Alfaify, H. Ghramh, M. I. Baig, Mohd Anis, *Material research innovations* (2017) 1 - 6. DOI: 10.1080/14328917.2017.1392694
- [5] H Pir, N Gu'nay, D Avc, Y Atalay, *Indian J Phys.*86 (2012) 1049 - 1063. DOI 10.1007/s12648 - 012 - 0171 - 6
- [6] Mohd Anis, S. S. Hussaini, M. D. Shirsat, *Optik* 127 (2016) 9734-9737. DOI: 10.1016/j.ijleo.2016.07.065

- [7] Mohd Anis, S. S. Hussaini, A. Hakeem, M. D. Shirsat, G. G. Muley, Optik 127 (2016) 2137–2142. DOI: **10.1016/j.ijleo.2015.11.097**
- [8] Min - hua Jiang, Qi Fang, Adv. Mater.11 (1999) 1147 - 1151. DOI: **10.1002/ (SICI) 1521 - 4095 (199909) 11: 13**
- [9] R. Sankar, C. M. Raghavan, R. Jayavel Cryst. Res. Technol.41 (2006) 919 - 924. DOI **10.1002/crat.200510696**
- [10] S. S. Kirupavathy, S. S. Mary, P. Srinivasan, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan, J. Cryst. Growth 306 (2007) 102 - 110. DOI: **10.1016/j.jcrysgro.2007.03.036**
- [11] J. Uma, V. Rajendran Ind. J. Comp. Appl.30 (2011) 8 - 10.
- [12] Mohd Anis, M. I. Baig, M. S. Pandian, P. Ramasamy, S. AlFaify, V. Ganesh, G. G. Muley, H. A. Ghramh, Cryst. Res. Technol. (2018). DOI: **10.1002/crat.201700165**
- [13] V. Ganesh, T. Bhaskar Rao, K. Kishan Rao, G. Bhagavannarayana, Mohd. Shkir Mater. Chem. Phys.137 (2012) 276 - 281. DOI: **10.1016/j.physb.2010.10.061**
- [14] Mohd Anis, S. S. Hussaini, M. D. Shirsat, G. G. Muley, Materials Research Innovations 20 (2016) 312 - 316. DOI: **10.1080/14328917.2015.1137693**
- [15] S. M. Azhar, MohdAnis, S. S. Hussaini, S. Kalainathan, M. D. Shirsat, G. Rabbani, Optics and Laser Technology 87 (2017) 11 - 16. DOI: **10.1016/j.optlastec.2016.07.007**
- [16] Mohd Anis, M. I. Baig, S. S. Hussaini, M. D. Shirsat, Mohd Shkir, H. A. Ghramh, Chin. Phys. B 27 (2018) 27800 - 27806.
- [17] Mohd Anis, M. I. Baig, M. S. Pandian, P. Ramasamy, S. AlFaify, V. Ganesh, G. G. Muley, H. A. Ghramh, Cryst. Res. Technol. (2018). DOI: **10.1002/crat.201700165**
- [18] Sauer M, Hofkens J, Enderlein J, Handbook of Fluorescence Spectroscopy and Imaging (Weinheim: Wiley - VCH) (2011).
- [19] Timothy H. Gfroerer, Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester (2000) 9209–9231.
- [20] Rupali Balwant Kulkarni, Mohd Anis, S. S. Hussaini, M. D. Shirsat, Mater. Res. Express in press. DOI: **10.1088/2053 - 1591/aab2f8**
- [21] Mohd Anis, M. S. Pandian, M. I. Baig, P. Ramasamy, G. G. Muley, Materials Research Innovations (2017). DOI: **10.1080/14328917.2017.1329992**
- [22] S. P. Ramteke, Mohd Anis, M. I. Baig, G. G. Muley, Optik154 (2018) 275–279. . DOI: **10.1016/j.ijleo.2017.10.047228**