Synthesis, Growth and Physicochemical Properties of Seminorganic NLO Crystal

Bis(Thiourea) Ammonium Nitrate

S.M. Ravi Kumar a*, A.Anbarasi b, S. Selvakumar c, and G.J. Shanmuga Sundar d

aDepartment of Physics, Government Arts College, Tiruvannamalai-606 603, Tamil Nadu, India

bDepartment of Physics, Periyar Government Arts College Cuddalore – 607 001, Tamil Nadu, India

cDepartment of Physics, Government Arts & Science College, Nandanam, Chennai-600 035, Tamil Nadu, India

dDepartment of Physics, Arignar Anna Government Arts College, Cheyyar-604 407, Tamil Nadu, India

*Corresponding Author: ravism23@gmail.com, smravi78@rediffmail.com

Abstract

Nowadays, NLO materials are of current research interest due to their variety of applications such as second harmonic generation, optical bi-stability, laser remote sensing, optical disk data storage, laser driver fusion, medical and spectroscopic laser, photonic integrated circuitry, optical parametric oscillations and THz wave generation. This work concentrated on (bis)thiourea ammonium nitrate (BTAN) crystal was grown from aqueous solution by slow evaporation technique. The grown crystal has been subjected to single crystal X-ray diffraction to determine the unit cell dimensions. The grown crystal was also characterized by recording the powder X-ray diffraction patterns and by identifying the diffracting planes. The Fourier Transform Infrared (FT-IR) spectra have been recorded in the range 400–4500 cm⁻¹. Second harmonic generation (SHG) for the materials of this work was confirmed using Nd:YAG laser. The UV–visible spectra show that the grown crystals have wide optical transparency in the entire visible region. The Thermo gravimetric/Differential Thermal Analyses reveal that the materials have good thermal stability.

Keywords: Slow evaporation, Semi organic, NLO crystal, UV-vis_NIR study, TGA and DTA

1 Introduction

Photonics and optoelectronics are fast developing fields and are mainly focusing on nonlinear optical (NLO) materials. NLO materials are widely used in various fields of optics and optoelectronics such as second harmonic generation, optical bi-stability, laser remote sensing, optical disk data storage, laser driven fusion, medical and spectroscopic laser, photonic integrated circuitry, optical parametric oscillations and THz wave generation [1-4]. Materials exhibiting large non linearity remains very active in research both basic and applied sciences [5]. In recent years, to achieve large charge transfer and the optical transparency with fewer dislocations density extensive efforts have been made to develop new inorganic, organic and semi-organic NLO crystals [6-8]. The selection of material may depend not only on laser conditions but also on the physiochemical properties such as molecular nonlinearity, transparency, and conversion efficiency and laser damage threshold [9, 10]. The strong delocalization of π electron in the organic back bone of semi-organic establishes higher molecular polarizability and hence electron
density takes place. This functionalizes both the ends of the \( \pi \) bond system with suitable electron donor and acceptor groups and enhances the asymmetric electronic distribution in both ground and excited states of semi-or ganics. This enables an increased optical nonlinearity by means of such as \( \pi \) delocalization length and donor acceptor groups with nonlinear optical function bonds [11]. Hence, the synthesis of novel efficient frequency conversion materials has resulted in the development of semi organic materials, which possess efficient physicochemical properties, such as large nonlinearity over a broad frequency range, high optical damage threshold, low angular sensitivity, low dielectric constant, mechanical stability and inherent synthetic flexibility [12-14]. Semi-organic crystals possess both the good qualities of organic and inorganic, it is used in device fabrication technology due to their enhanced physiochemical properties such as thermal stability, wide range of transparency and excellent NLO coefficient [15, 16].

The NLO properties of semi organic crystals have attracted significant attention in the last few years, because both organic and inorganic components in it contribute specifically to process of second harmonic generation (SHG). Particularly, thiourea complex semi organic crystals are shows good second harmonic generation (SHG) efficiency. Thiourea molecules are an interesting in organic matrix modifier due to its large dipole moment and its ability to form and extensive network of hydrogen bonds [17]. The Centro symmetric thiourea molecule, when combined with inorganic salt yield non- centro symmetric complex, which has the nonlinear optical properties [18]. Hence, in the present study concentrated on synthesis, growth, structural, optical, SHG and thermal properties of thiourea complex semi organic crystal namely bis(thiourea) ammonium nitrate (BTAN) and the results are reporting for the first time.

2 EXPERIMENTAL PROCEDURES

Thiourea and ammonium nitrate supplied by Merck, India, were used without further purification. Thiourea mixed with ammonium nitrate in molar ratio 2:1. The saturated solution of ammonium nitrate was slowly added to the saturated solution of thiourea at room temperature and it has been stirred well for nearly 8 hours to obtain the homogenous solution. The solution of title compound was synthesis by the following chemical reaction.

\[
2[CH_4N_2S] + NH_4NO_3 \rightarrow NH_4(CH_4N_2S)_2 NO_3
\]

The saturated solution was filtered using Wattman filter paper. The filtered solution was taken in a beaker and covered with good quality perforated polythene cover to restrict the fast evaporation and it’s kept at room temperature in a dust free compartment for slow evaporation. After the period of 40-60 days, colorless crystals with dimension 10mm x 6mm x 3mm were harvested. The grown crystals are non-hygroscopic and optically good transparent in nature. Well-faced good quality crystals of BTAN are shown in the figure 1.
3. Results and Discussion

The title compound was analyzed by single crystal XRD by ENRAF NONIUS CAD4-F single X-ray diffractometer with MoKα(λ=0.717 Å) radiation. It is observed that the grown crystal crystallizes in orthorhombic system with space group P21. The calculated lattice parameter for BTAN was found to be a = 8.73 Å, b = 9.90 Å, c = 12.64 Å and volume, V = 1092 Å³.

The powder sample of grown crystal has subjected to Powder X-ray diffraction by using BRUCKER, Germany (model D8 Advance) X-ray diffractometer with CuKα (wavelength = 1.5405 Å) radiation. The Powder X-ray diffraction pattern of BTAN crystal was recorded at specific 20 angles and also powder sample was scanned over the range 10° to 80° at a scan rate of 1° / min. The well defined peaks are reveals that the grown crystal has good quality and high crystalline nature. The observed powder XRD pattern of BTAN crystal is shown in the Figure 2.
Figure 2 Powder X-ray diffraction (PXRD) Analysis of BTAN

The FTIR spectroscopy study effectively used to identify the presence of various functional groups presence in the materials. Figure 3 shows the FTIR spectrum of BTAN.

Figure 3 FTIR Spectrum of BTAN Crystal
The observed peak at 3410 cm$^{-1}$ and 3183 cm$^{-1}$ may be due to NH$_2$ stretching and N-H symmetric stretching vibrations respectively. The above mentioned peaks are the characteristic vibrations of thiourea and hence confirm the thiourea molecule in the grown crystal. The peaks at 2977 cm$^{-1}$ is due to C-H stretching vibration. The NH$_2$ bending vibration is observed around 1620 cm$^{-1}$. The peaks at 1383 cm$^{-1}$ confirm the C=S stretching vibration. The C-H deformation was observed at 666 cm$^{-1}$. The peak at 588 cm$^{-1}$ is due to N-C-N stretching. The observed wave number and corresponding assignments of BTAN crystal is compare with thiourea is given in Table 1.

| Wavenumber (cm$^{-1}$) | Assignment                  |
|------------------------|-----------------------------|
| 3380                   | NH$_2$ asymmetric stretching |
| 3179                   | N-H symmetric stretching    |
| 3090                   | C-H stretching vibration    |
| 1627                   | NH$_2$ bending              |
| 1412                   | Symmetric C-N stretching    |
| 740                    | Symmetric C=S stretching    |
| 494                    | N-C-N Stretching            |

Table 1 Comparison of FTIR assignments of thiourea and BTAN crystal

The suitable dimension and well polished crystal of BTAN was used for absorption study. A spectrum was recorded in the region 100-1000nm using VARIAN CARY 5E model spectrophotometer. The absorption spectrum obtained is shown in the Figure 4.
The absorbance is found to be low throughout the entire visible and near IR region due to the delocalization of electronic cloud through charge transfer axis. This is the most desirable property of the materials possessing NLO activity. The crystal shows good transmittance in the visible region and the lower cut off wavelength found to be 280nm. It is well known that the crystal has low cut off wavelength lies between 200 to 400 nm, suitable for device fabrication and more NLO applications. Hence, BTAN crystal is a suitable potential candidate for NLO applications.

Kurtz-Perry Powder second harmonic generation (SHG) measurements [25] was carried on grown crystal of BTAN using a a spectra-physics quanta-ray prolab 170 Nd:YAG laser with the first harmonics input at 1064nm and a pulse width of 10ns at repetition rate of 10Hz. This measurement offers possibility of assessing the nonlinearity of new materials. The grown crystal was identified as a NLO crystal due to the emission of high intense green radiation. Also the SHG efficiency was found to be 11.82 mJ. This value is compare with known NLO crystal of KDP which has the SHG efficiency 7.80 mJ. Hence, the SHG efficiency of BTAN is 1.52 times greater than that of KDP crystal. Therefore, BTAN crystal is a suitable candidate for device and various technological applications.

Information regarding phase transition and different stages of decomposition of the grown crystal BTAN crystal were identified by DTA and TGA thermal studies. BTAN crystal was weighed in an Al2O3 crucible with microprocessor temperature control system. DTA and TG curve of grown crystals were plotted in nitrogen atmospheres between ambient temperatures 100 to 1232 °C shown in the figure 5.
Figure 5. DTA and TG curve of BTAN crystal

There is no weight loss up to 184.05 °C indicating that there is no inclusion of water in the crystal lattice. The recorded thermogram reveals that the major weight loss starts at 184 °C and continues up to 1232 °C. It is further observed that the DTA curve shown that first endo thermionic peak at 184 °C is assigned to melting point of the BTAN compound and the remains exo thermionic peaks at 221 °C, 232 °C, 235 °C, 266 °C and 290 °C are indicate the changes in the physical state of the crystal. The nature of the weight loss and sharpness of the peak ensure the decomposition and purity with crystalline nature of the material respectively. The observed decomposition point of BTAN crystal 184 °C indicates that BTAN crystal is thermally stable up to 184 °C.

4. Conclusion

Optically good crystals of (bis)thiourea ammonium nitrate has been grown from aqueous solution by slow evaporation technique under room temperature. Single crystal XRD analysis confirmed that the BTAN crystallize in orthorhombic system. Powder X-ray diffraction study revealed the crystalline nature of grown crystal. The optical quality of the grown crystal was justified by optical absorption studies. The sharp absorption on set at 280 nm and high absorption values of the grown crystal at wavelength above 380 nm, exhibit the optical quality. The powder SHG measurement shows the grown BTAN crystal having SHG efficiency of about 1.52 times that of KDP crystal. Thermal stability
of grown sample was studied by TGA and DTA analyses which reveal that the BTAN crystal thermally stable up to 184 °C.

Acknowledgement

The authors thank B. S. Abdur Rahman University, Vandalur, Chennai for providing instrument facility for characterization and also the corresponding author thankfully acknowledge the Science and Engineering Research Board (SERB), Department of Science and Technology (DST) for the financial support for Project (FILE NO.EEQ/2016/000451).

References

1. Santhanu Bhattacharya, Parthasarathi, Dustidar, T.N. Guru Row, Chem. Mater. 61, 531 (1994).
2. T.Kaino, B.Cai, T.Takayama, Adv. Funct. Mater. 12, 599 (2002).
3. M.Thakur, J.Xu, A.Bhowmilk, L.Zhou, Appl. Phys. Lett. 74, 635 (1999).
4. A. Schneider, M.Neis, M.Stillhart, B.Ruiz, R.U.A.Khan, P.Gunter, J.Opt. Soc. Am. B23, 1822 (2006).
5. R.J.Collins, D.F.Nelson, A.L.Schawlow, W.Bond, C.G.B.Garrett, W.Kaiser, Phys. Rev. Lett. 5, 303 (1960).
6. Xiue Ren, Dongli Xu, Dongfeng Xue, J.Crystal Growth, 310, 2005 (2008).
7. Dongfeng Xue, Henryk Ratajczak, Chem. Phys. Lett. 371, 601 (2003).
8. Dongfeng Xue, Siyuan Zhang, Chem. Phys. Lett. 301, 449 (1999).
9. F.Zernike, J.E.Midwinter, in:Applied nonlinear optics, Wiley, Newyork, (1973).
10. P.N.Prasad, D.J.Willams, in:Introduction to nonlinear efforts in molecules and polymers, Wiley, New York (1991).
11. Daqiu Yu, Dong feng Xue, Henryk Ratajczak, J.Mol. Stuct. 792 (2006) 280-285.
12. Y.R.Shen, The principles of nonlinear optics, Wiley, New York (1984).
13. H.O. Marcy, L.F. Warren, M.S.Webb, C.A.Ebbers, S.P.Velsko, G.C.Kenndy, Appl. Opt. 31, 5051 (1992).
14. S.Ledoux, J.Zyss, J. Int. Nonlinear opt. Phys. 3, 287 (1994).
15. S.M. Ravi Kumar, N. Melikechi, S. Selvakumar, P. Sagayaraj, Physica B: Condensed Matter 403, 4160 (2008).
16. S. Selvakumar, S.M. Ravi Kumar, Ginson P. Joseph, K. Rajarajan, J. Madhavan, S.A. Rajasekar, P. Sagayaraj, Materials Chemistry and Physics, 103 (1), 153 (2007).
17. K.H. Hellwege, A.M. Hellwage, *Landolt-Bornstein Group II* 14, 584 (1982).
18. M. Lawrence, J. Thomas Joseph Prakash, *Spectrochim. Acta Part A*, 91, 30 (2012).