Journal of Alloys and Compounds 509 (2011) 4543–4546

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis, optical and dielectric studies on novel semi organic nonlinear optical crystal by solution growth technique

V. Chithambaram [a], S. Jerome Das [b], S. Krishnan [c,*]

[a] Department of Physics, AMET University, Kanathur, Chennai 603112, India
[b] Department of Physics, Loyola College, Chennai 600 034, India
[c] Department of Physics, R. M. K. Engineering College, Kavaraipettai 601206, Chennai, India

ARTICLE INFO

Article history:
Received 26 July 2010
Received in revised form 17 January 2011
Accepted 18 January 2011
Available online 22 January 2011

Keywords:
Optical materials
Crystal growth
Nonlinear optics
X-ray diffraction

ABSTRACT

Bisthiourea lead acetate $Pb[SC(NH_2)_2]_2(CH_3COO)_2$, a novel semi organic non linear optical crystal having dimensions 17 mm × 2 mm × 2 mm were grown using slow evaporation technique. The lattice parameters for the grown crystals were determined using single crystal XRD. The presence of functional groups for the grown crystals was confirmed using Fourier transform infrared (FT-IR) spectroscopy. The optical absorption studies show that the material has wide optical transparency in the entire visible region. The dielectric constant and dielectric loss has been studied as a function of frequency for various temperatures and the results were discussed in detail. The second harmonic generation was confirmed by Kurtz powder method and it is found to be 5 times than that of potassium dihydrogen phosphate (KDP) crystal.

1. Introduction

In recent years, second order nonlinear optical materials have attracted many researchers because of their potential applications in various emerging technological fields [1–7]. Today, crystal growth technology has advanced rapidly for the development of novel nonlinear optical materials (NLO) for various applications such as optical switching, frequency conversion and electro-optical modulation [8–13]. The organic NLO materials have large nonlinear optical coefficients compared to inorganic material, but their use is impeded by their poor mechanical and thermal properties and low laser damage threshold [14]. The inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to lack of extended π-electron delocalization [15]. In view of these problems, a new class of materials has been developed from organic and inorganic complexes called semi organic [14,16]. In these materials, high optical nonlinearity of pure organic compound is combined with the favorable mechanical and thermal properties of inorganic materials [14–18]. Semi organic crystals have large damage threshold, wide transparency range, less deliquescence, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [19–22].

In the present work, bisthiourea lead acetate (BTLA), a desirable semi organic nonlinear optical crystal, has been grown from aqueous solution using slow evaporation technique. The grown crystals were subjected to various characterizations such as single crystal X-ray diffraction analysis, Fourier transform infrared (FTIR) analysis, optical absorption studies, dielectric studies and nonlinear optical studies and were discussed in detail.

2. Experimental

2.1. Materials

(AR grade) thiourea and lead acetate purchased from Merck were used to synthesis the crystal. Triple distilled water was used as solvent.

2.2. Crystal growth

Single crystals of BTLA were grown by dissolving (AR grade) thiourea and lead acetate in the ratio 2:1 using triple distilled water. The chemical reaction is as follows.

$$(CS(NH_2)_2)_2 + Pb(CH_3COO)_2 \rightarrow Pb[SC(NH_2)_2]_2(CH_3COO)_2)$$

Extreme care was taken to minimize the thermal and mechanical disturbances to the supersaturated solution. After recrystallisation and filtration, optically good quality and needle shaped crystal having dimensions 17 mm × 2 mm × 2 mm was obtained within a period of 6 weeks. The photograph of the grown crystal is shown in the Fig. 1.

* Corresponding author. Tel.: +91 44 27925102; fax: +91 44 27925193.
E-mail address: skrishnanjp@gmail.com (S. Krishnan).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.091

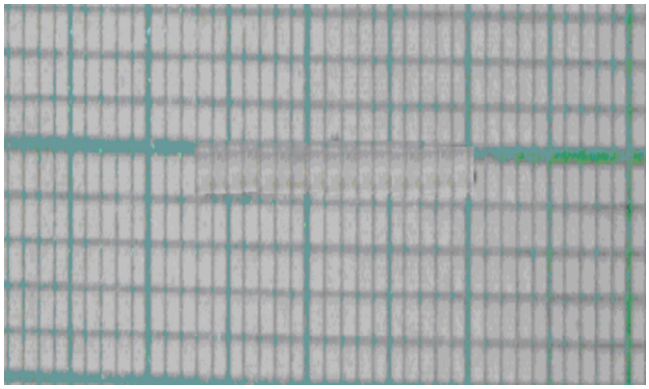

Fig. 1. Photograph of as grown crystal of BTLA.

3. Results and discussion

3.1. Single crystal X-ray diffraction

The grown crystals were subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffractometer to determine the cell parameters and it reveals that the BTLA crystal crystallizes in monoclinic system having non-centrosymmetric space group P_{21}. The lattice parameters were found to be $a = 4.567(3)$ Å, $b = 15.827(7)$ Å, $c = 13.744(5)$ Å, $\beta = 92.44(4)^\circ$ and $V = 992.53$ Å^3.

3.2. FTIR analysis

The FTIR spectrum of the grown crystals was recorded in the range 400–4000 cm^{-1} using IFS BRUKKER 66 V spectrophotometer and the resultant spectrum is shown in the Fig. 2. The symmetric and asymmetric C═S stretching vibrations of thiourea are observed at 719 cm^{-1}. The COH stretching mode occurred at 1046 cm^{-1} in the spectrum. The absorption band at 1532 cm^{-1} is due to NH_2 in group deformation. The C═H valence and C≡H valence of thiourea are observed at 3191 cm^{-1} and 3304 cm^{-1} respectively. The C≡H symmetrical band is assigned at 3373 cm^{-1} in the spectrum. The symmetric NH_2 stretching is assigned at 3304 cm^{-1}. The absorption band at 1630 cm^{-1} shows the functional group NH_2 in bending mode. The absorption band at 1409 cm^{-1} can be assigned to C═S stretching vibration. The sharp and intense peak at 670 and 719 cm^{-1} attributed to double bond character of the C═S band on coordination. The band at lower frequency 550 cm^{-1} is attributed to asymmetric N–C–N bending vibration. The symmetric and asymmetric stretching of COO^- is found to be at 1409 and 1532 cm^{-1} respectively. The symmetrical CH_3 bending can be assigned at 1333 cm^{-1}. The symmetrical C–C stretching is found to be at 925 cm^{-1}. The OCO bending is found to be at 670 cm^{-1}. The characteristic vibrational frequencies of the functional groups of BTLA have been compared with pure thiourea [23,24]. This confirms the presence of metal acetate in the crystal lattice of thiourea. The comparison of characteristic vibrational frequencies has been tabulated in Table 1.

Table 1
Comparison of IR bands of BTLA with thiourea.

Thiourea (cm^{-1})	BTLA (cm^{-1})	Assignment
469	487	δs(S–C–N)
494	550	δas(N–C–N)
740	719	νs(C═S)
1089	1125	νs(C–N)
1417	1409	νas(C═S)
1627	1630	δ(NH2)
3280	3299	νs(NH2)
–	3414	νas(NH2)

3.3. Optical absorption studies

The optical absorption spectrum for the grown crystals was recorded in the range 200–2000 nm using VARIAN CARY 5E SECTROPHOTOMETER and is shown in the Fig. 3. The resultant spectrum shows that the crystal has very low absorbance in the entire visible and IR region. The UV cut-off wavelength is found to be at 320 nm. This very low absorption property of the grown crystal in the entire visible region suggests its suitability for second harmonic generation [25,26].

The optical absorption coefficient (α) was calculated from the transmittance using the following relation,

$$\alpha = \frac{1}{t} \log\left(\frac{1}{T}\right) \quad (1)$$

where T is the transmittance and t is the thickness of the crystal.

As a direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon

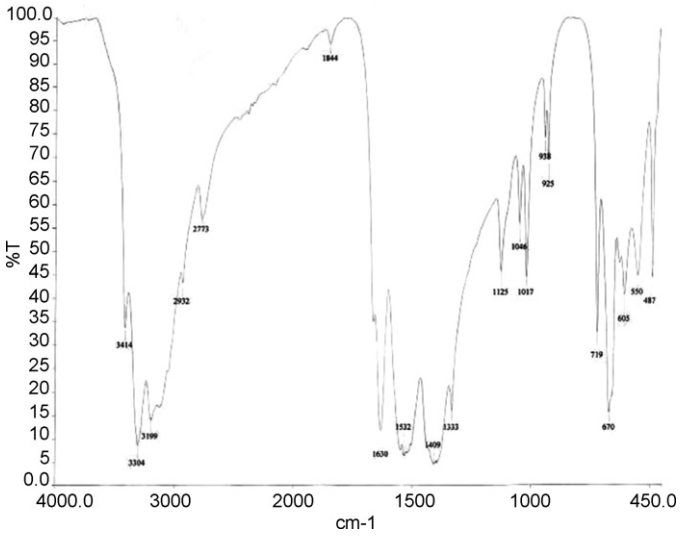

Fig. 2. FT-IR spectrum of BTLA crystal.

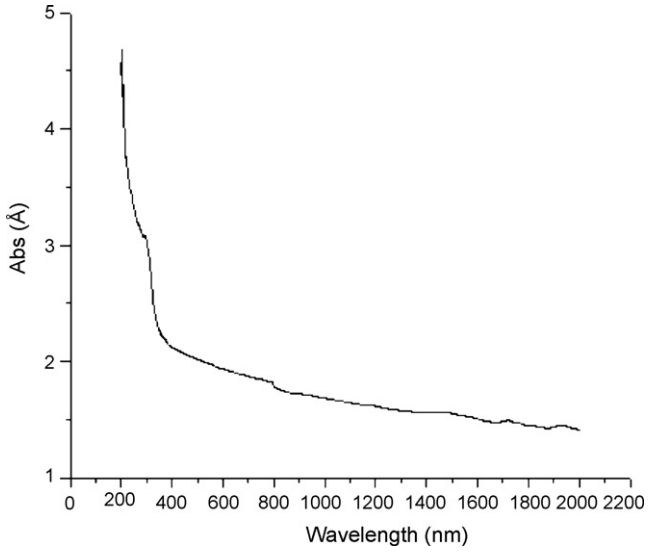

Fig. 3. Optical absorption spectrum of the BTLA crystal.

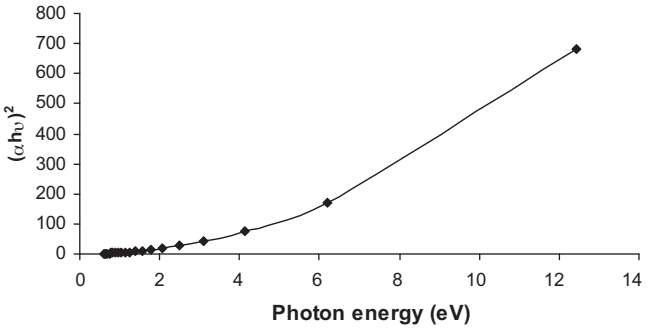

Fig. 4. Plot of variation of $(\alpha h\mu)^2$ vs. $h\mu$.

energies ($h\nu$):

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (2)$$

where E_g is the optical band gap of the crystal and A is a constant. The plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 4. E_g is evaluated using extrapolation of the linear part [27]. The energy absorption gap is of direct type and the band gap energy is found to be 3.3 eV. As a consequence of a wide band gap, the grown crystal has a large transmittance in the visible region [28].

3.4. Dielectric studies

An optically good quality single crystal of BTLA was selected for dielectric measurements using HIOKI 3532-50 LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil. Silver paint was applied on the both faces to make a capacitor with the crystal as a dielectric material. The dielectric constant is calculated using the relation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (3)$$

where C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of the free space (8.854×10^{-12} F/m). The variation of dielectric constant (ε') was studied as a function of frequency for the grown crystal at various temperatures viz., 308, 323, and 338 K and is shown in Fig. 5. The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually [29]. From the plot, it is also observed that dielectric constant decreases with increase in frequency. The variation of dielectric loss with frequency is shown in Fig. 6. The characteristics of low dielectric loss at very high frequency suggest that it possesses enhanced optical quality with lesser defects and this parameter is essential for nonlinear optical applications [30].

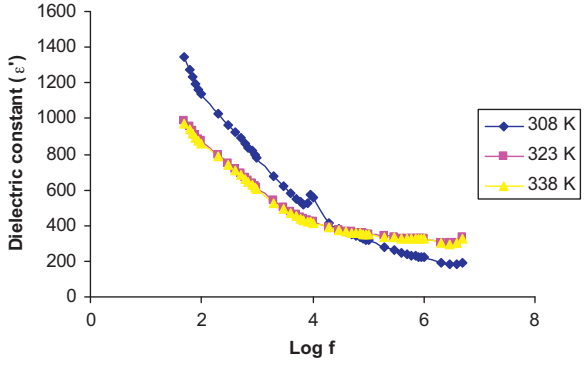

Fig. 5. Variation of dielectric constant vs. log f.

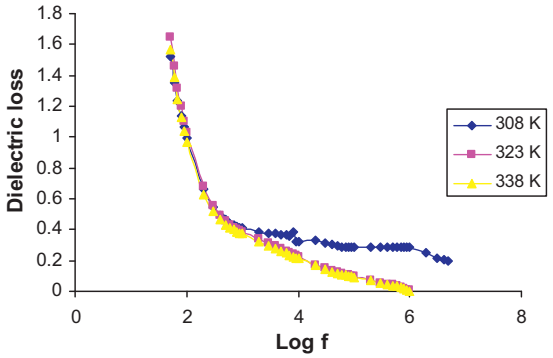

Fig. 6. Variation of dielectric loss vs. log f.

3.5. Kurtz powder SHG test

The second harmonic generation efficiency measurement was carried out on the grown crystal using the Kurtz–Perry powder technique. The crystal was grounded into a homogenous powder of particles and densely packed between two transparent glass slides. The powder sample with average particle size 100–115 μ were illuminated using Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm with the pulse width of 8 ns. The second harmonic generations was confirmed by the emission of green radiation (532 nm). The output power is found to be 5 times than that of KDP.

4. Conclusions

Optically transparent single crystals of BTLA were grown from aqueous solution using slow evaporation technique. Single crystal X-ray diffraction analysis confirms that the grown crystals crystallize in monoclinic system having space group P_{21}. FTIR analysis confirms the presence of lead acetate in the crystal lattice of thiourea. The UV cut-off wavelength is found to be at 320 nm and the band gap energy is found to be 3.3 eV. Dielectric constant decreases with increase in frequency and very low values of dielectric loss infer very high purity of the crystal. NLO studies confirm that the SHG efficiency of BTLA is 5 times than that of KDP crystal. All these studies indicate that the BTLA crystal can be considered as a potential candidate for the fabrication of optoelectronic devices.

Acknowledgements

The scientific supports extended by Sophisticated Analytical Instruments Facility, Indian Institute of Technology, Chennai and Indian Institute of Science (IISc) are gratefully acknowledged. The encouragement and support rendered by Prof. G. Selvakumar, Head, Department of Physics, AMET University is gratefully acknowledged.

References

[1] C. Zhang, Z. Li, H. Cong, J. Wang, H. Zhang, R.I. Boughton, Journal of Alloys and Compounds 507 (2010) 335–340.
[2] S. Arjunan, A. Bhaskaran, R. Mohan Kumar, R. Mohan, R. Jayavel, Journal of Alloys and Compounds 506 (2010) 784–787.
[3] R. Uthrakumar, C. Vesta, G. Bhagavannarayana, R. Robert, S. Jerome Das, Journal of Alloys and Compounds 509 (2011) 2343–2347.
[4] Mohd. Shakir, B. Riscob, K.K. Maurya, V. Ganesh, M.A. Wahab, G. Bhagavannarayana, Journal of Crystal Growth 312 (2010) 3171–3177.

[5] P.V. Dhanaraj, N.P. Rajesh, G. Bhagavannarayana, Physica B: Condensed Matter 405 (2010) 3441–3445.
[6] P. Maadeswaran, J. Chandrasekaran, S. Thirumalairajan, Optik – International Journal for Light and Electron Optics 122 (2011) 259–262.
[7] T. Baraniraj, P. Philominathan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 75 (2010) 74–76.
[8] G.A. Babu, A. Chandramohan, P. Ramasamy, G. Bhagavannarayana, B.Varghese, Materials Research Bulletin, in press.
[9] M. Roth, M. Tseitlin, Journal of Crystal Growth 312 (2010) 1059–1064.
[10] M.K. Gupta, N. Sinha, B. Kumar, Physica B: Condensed Matter 406 (2011) 63–67.
[11] A. Bhaskaran, C.M. Raghavan, R. MohanKumar, R. Jayavel, Current Applied Physics 10 (2010) 1261–1266.
[12] J.M. Linet, S.J. Das, Materials Chemistry and Physics, in press.
[13] S.-H. Jang, A.K.-Y. Jen, Comprehensive Nanoscience and Technology 6 (2011) 143–187 (Chapter 1).
[14] M.-h. Jiang, Q. Fang, Advanced Materials 11 (1999) 1147–1151.
[15] J. Ramajothi, S. Dhanuskodi, K. Nagarajan, Crystal Research Technology 39 (2004) 414–420.
[16] S. Ariponnammal, S. Radhika, R. Selva, N. Victor Jeya, Crystal Research Technology 40 (2005) 786–788.
[17] M.J. Rosker, P. Cunningham, M.D. Ewbank, H.O. Marcy, F.R. Vachss, L.F. Warren, R. Gappinger, R. Borwick, Pure Applied Optics 5 (1996) 667–680.
[18] K. Selvaraju, R. Valluvan, K. Kirubavathi, S. Kumararaman, Optics Communication 269 (2007) 230–234.
[19] J.M. Linet, S. Dinakaran, S.J. Das, Journal of Alloys and Compounds, in press.
[20] M. Esthaku Peter, P. Ramasamy, Journal of Crystal Growth 312 (2010) 1952–1956.
[21] T.C. Sabari Girisun, S. Dhanuskodi, D. Mangalaraj, J. Phillip, Current Applied Physics, in press.
[22] S. Dinakaran, S. Verma, S. Jerome Das, S. Kar, K.S. Bartwal, Crystal Research and Technology 45 (2010) 233–238.
[23] P. Angeli Mary, S. Dhanuskodi, Crystal Research Technology 36 (2001) 1231–1237.
[24] N.R. Dhumane, S.S. Hussaini, V.V. Nawarkhele, M.D. Shirsat, Crystal Research Technology 41 (2006) 897–901.
[25] S.A. Roshan, C. Joseph, M.A. Ittyachen, Material Letters 49 (2001) 299–302.
[26] V. Venkataramanan, S. Maheswaran, J.N. Sherwood, H.L. Bhat, Journal of Crystal Growth 179 (1997) 605–610.
[27] A.K. Chawla, D. Kaur, R. Chandra, Optics Materials 29 (2007) 995–998.
[28] D.D.O. Eya, A.J. Ekpunobi, C.E. Okeke, Academic Open Internet Journal 17 (2006).
[29] C.P. Smyth, Dielectric Behavior and Structure, McGraw-Hill, New York, 1965, p. 132.
[30] C. Balarew, R.J. Duhlew, Solid State Chemistry 55 (1984) 1–6.