Spectral, dielectric and optical properties of urea barium chloride nonlinear optical crystals

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Semi-organic nonlinear optical crystal of urea barium chloride has been grown from aqueous solution by slow evaporation technique at room temperature. EDAX analysis was carried out to identify the constituent elements present in the as grown crystal sample. The grown crystals were characterized by using powder X-ray diffraction analysis. The grown crystal was subjected to single-crystal X-ray diffraction analysis to find the lattice parameter and system of the crystal. The vibrational frequencies of various functional groups were confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. The UV–vis–NIR spectrum of the crystal shows the lower cut-off wavelength at 320 nm. The dielectric properties were studied at room temperature. The optical behavior, including second harmonic generation (SHG), was investigated to study its NLO property and compared with KDP.

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1. Introduction

The search for new nonlinear optical (NLO) materials has been the subject of intense research. Materials with large second-order nonlinearities, large optical transmission window and stable physicochemical performance are needed for various applications [1, 2]. To answer these requirements, organo-metallic and coordination complex materials share the properties of both organic and inorganic materials perform large nonlinearity, high resistance to laser induced damage, low angular sensitivity, good dielectric effects and good thermal stability and mechanical hardness [3-6]. In this connection, urea is a noticeable material owing to competent nonlinear optical efficiency. Urea is one of the organic crystals and it has large nonlinear optical coefficients, a high birefringence and a high laser damage threshold. It is one of the most promising materials for nonlinear optical applications in UV because of its transparency range extending to 200 nm in the short wavelength limit [7]. Some of the semi-organic NLO crystals have been reported earlier based on the organic with inorganic salts like, urea L-histidine bromide [8], urea thiourea cadmium chloride [9], ammonium chloride-doped urea L-malic acid [10], urea L-malic acid [11], urea thiourea zinc chloride [12], glycine barium dichloride [13], barium thiourea chloride[14], L-proline barium chloride monohydrate [15] and L-alanine barium chloride [16]. So crystals of semi-organic compounds are subjected to extensive investigation for nonlinear optics. In the present paper consist of, urea is combined with barium chloride to form a semi-organic nonlinear optical material and systematic investigation has been carried out on the growth of UBC crystal. The grown samples are subjected to various characterizations such as single crystal XRD, Powder XRD, FTIR, optical property, dielectric studies and NLO test.

2. Experimental technique

2.1. Materials synthesis

The starting material was synthesized by taking urea and barium chloride in a 1:1 stoichiometric ratio. The required amount of starting materials for the synthesis of UBC crystal was calculated. The calculated amount of barium chloride was first dissolved in deionized water. Urea was then added to the solution. The solution was agitated with a magnetic stirring device for 10hrs continuously and filtered after complete dissolution of the starting materials.

2.2. Crystal growth

The saturated solution of UBC crystal was prepared at room temperature. The solution was then filtered twice to remove the suspended impurities. The prepared solution was allowed to evaporate at room temperature and crystal of good optical quality was harvested from the solution within a period of 29 days, as shown in Fig. 1. The grown crystal of size 20 ×4 ×3 mm^3 of UBC has been grown by slow evaporation method. Urea reacts with barium chloride as following Eqn. (1).

$$CH_4N_2O+BaCl_2 = Ba.(CH_4N_2O).Cl_2 \qquad (1)$$

Fig. 1. Photograph of grown UBC crystal

3. Results and discussion

3.1. EDAX analysis

EDAX analysis was carried out to find the constituent elements present in the as grown UBC crystal sample. For this analysis, JEOL model JED-2300 instrument was used to record the EDAX spectrum.

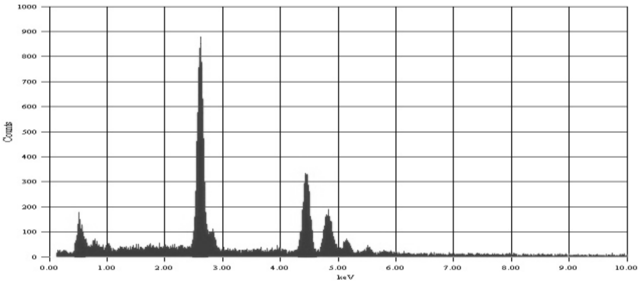

Fig. 2. EDAX spectrum of UBC crystals.

The presence of the constituent elements of C (3.42%), H (1.58%), N (9.20%), O (6.10%), Ba (52.2%) and Cl (27.5%) were confirmed by the occurrence of their respective peaks in the recorded spectrum as shown in Fig. 2. From this analysis, we confirmed the presence of barium and chloride in grown crystal [17].

3.2. Powder XRD analysis

The purified samples of the grown crystals were crushed to a uniform fine powder and subjected to powder X-ray diffraction using Bruker AXS D8 advance powder diffractometer with Cu, Wavelength 1.5406Å. The specimen was scanned in the reflection mode in the 2θ range 10–80°.

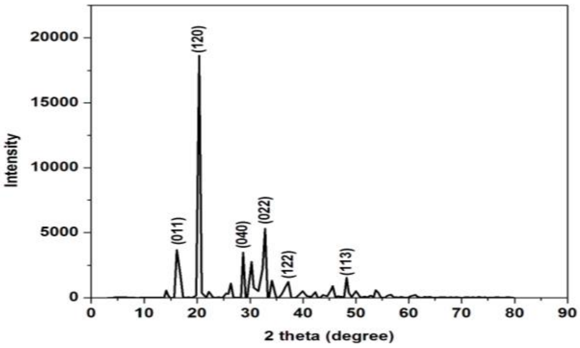

Fig. 3. Powder XRD patterns of UBC crystal.

All the observed prominent peaks in XRD patterns were indexed as shown in Fig. 3. The results of well defined diffraction peaks at specific 2θ angles of grown crystal is well shifted with compared of pure urea. This may be due to the presence of barium chloride [18]. The well defined diffraction peaks confirm purity and better crystallinity of the sample.

3.3. Single crystal XRD analysis

The unit cell parameters were determined from the single-crystal X-ray diffraction data obtained with a four-circle Nonius CAD4 / diffractometer (MoKα, λ = 0.71073 Å). The lattice cell parameters are a=6.7167(7) Å, b=10.9058(10) Å, c=7.1279(7) Å, β=91.1(2)° and volume V=522.03(9) Å^3 and the grown crystal belongs to $P2_1$ space group, which is known as non-centrosymmetric vital requirements for the SHG activity of the crystal. The lattice parameter of the pure urea has been reported earlier by Gora *et al* [19]. The lattice cell parameters of UBC crystal are shifted to high value when compared to pure urea crystals. The grown crystal is belongs to monoclinic system.

3.4. FTIR spectral analysis

The FTIR spectrum of UBC crystals was recorded using a thermo Nicolet, Avatar 370 spectrometer in the wavelength range of 400–4000 cm^{-1}. The infrared spectral analysis was carried out to understand the chemical bonding of the compound. The resulting spectrum of the crystal is shown in Fig. 4. Infrared spectral analysis was carried out to identify with the chemical bonding and it provides practical information regarding the molecular structure of the compound. The high frequency of N-H absorption bands in the region 3100-3500 cm^{-1} in the spectra of urea were shifted to higher frequencies on the formation of inorganic compound. The small bands of N-H stretching of pure urea are observed at 3422 and 3320 cm^{-1} can be shifted to 3465 and 3312 cm^{-1} respectively due to the presence of barium compound. FTIR spectrum of pure urea crystal has been reported by Madhurambal *et al* [20]. A small hump shifted around 1750 cm^{-1} is due to C–H stretching [7]. In addition, stretching frequency of NH_2 is shifted from 1631 cm^{-1} to 1602 cm^{-1}. The C–N stretching frequency of pure urea appears at 1454 cm^{-1} is shifted to 1433 cm^{-1}. The combination band of grown crystal is indicating at 1369 cm^{-1}. The N-C-N symmetry stretching of pure urea is assigned as 1008 cm^{-1} is moved to 1018 cm^{-1}. A peak at 790 cm^{-1} shifted to 810 cm^{-1} is assigned as C=S stretching. The N-C-S stretching of 508 cm^{-1} is shifted to 563 cm^{-1}. The modify frequencies are indicated the presence of barium chloride in the grown crystal. The results are presented in Table 1.

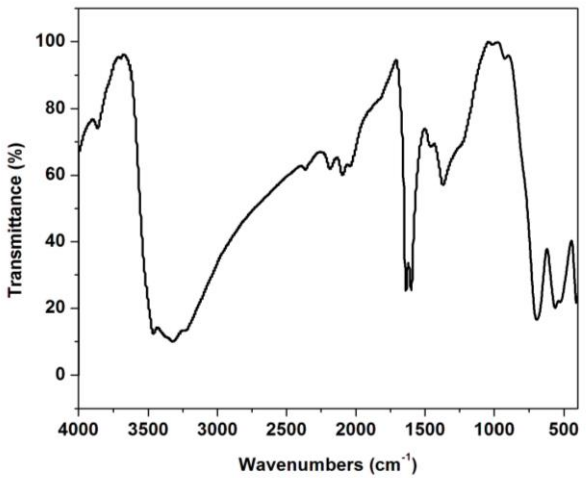

Fig. 4. FTIR Spectrum of UBC crystal

Table 1. Assignments of vibrational frequencies

Pure urea Wave number (cm^{-1}) [12]	UBC wave number (cm^{-1})	Assignments
3422	3465	NH stretching
3320	3312	NH stretching
1631	1602	NH_2 stretching
-	1612	NH_2 plane bending
1454	1433	C-N stretching
-	1442	N-C-N asymmetric stretching
1162	1199	C=S stretching
-	1135	NH_2 rocking structure
1008	1018	C-N stretching
790	810	C=S stretching
508	563	N-C-S stretching

3.5. UV-vis-NIR spectrum

Optical transmission spectrum was recorded using (Varian, Cary 5000) in the range of 200-1100 nm. The transmittance nature of the crystals found to be in the entire visible and IR region is a desirous property of this material for NLO applications. A graph of transmittance Vs wavelength (nm) is shown in Fig. 5. There is no significant absorption in the range between 550-1100 nm indicate the use of organic compound where the absence of strongly conjugated bonds leads to wider transparency range in the UV spectral regions. The lower cut off wavelength of pure urea has 335 nm reported earlier [20]. From the UBC spectrum, it is evident that the crystal has lower cut off wavelength at 320 nm and it is being lesser than that of pure urea. The grown crystal shows 80% transparency, which makes it an extremely potential material for NLO applications.

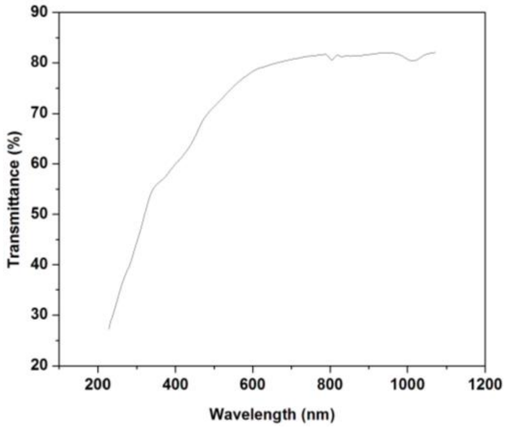

Fig. 5. Optical transmittance spectrum of UBC crystal.

3.6. Fluorescence studies

The emission and excitation spectra of the crystals are recorded by using Model: FLUOROLOG - FL3-11 spectroflurometer.

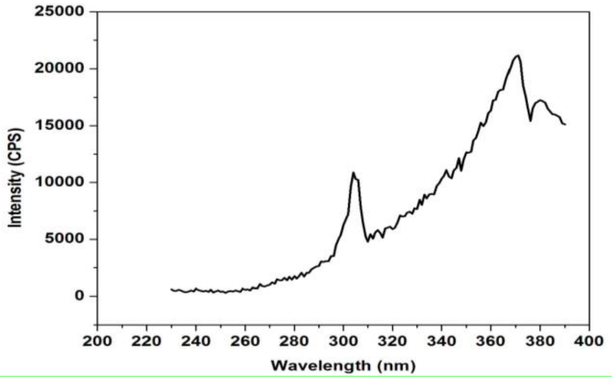

Fig. 6. Emission spectrum of UBC crystal

The band gap energy at this peak was calculated using the formula $E_g = hc/\lambda e$. Here h, c, and e are constant where λ is the wavelength of fluorescence. The band gap energy calculated is about 3.356 eV (at 370 nm). The emission spectrum was recorded in the range of 230 to 390 nm. From the emission spectrum (Fig. 6), intensity peaks at 309 nm and 370 nm are observed. This intensity is slowly reduced in the higher wavelength due to the presence of electron donating group NH and electron-withdrawing group COOH that can enhance the mobility of π electrons.

3.7. Microhardness study

The microhardness study was carried out to determine the mechanical strength of the grown crystals using HMT 2T, SHIMADZU Vickers microhardness tester. The indentation marks were made on the surface of the crystals at room temperature by applying load of 25, 50 and 100 g.

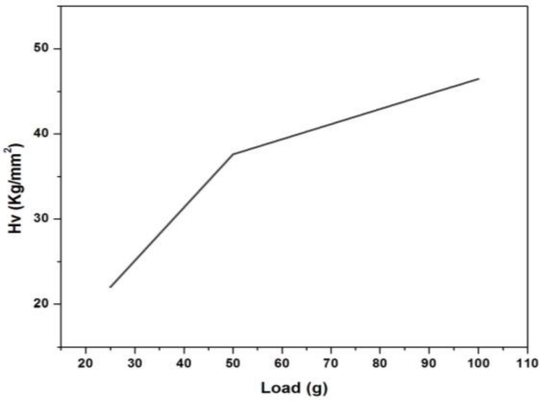

Fig. 7. Plot of load (Vs.) hardness for UBC crystal

The H_v was found to increase with the increase in the load from 25 to 100 g and crack occurred at higher loads. A graph (Fig. 7) has been plotted between H_v and applied load P. The hardness number (H_v) of the crystal was calculated using the relation H_v=1.8544 P/d^2 (kg/mm^2); here, H_v is the Vickers hardness number in kg/mm^2, P is the applied load in kg and d is the average diagonal length of the indentation in mm. From the graph it can be observed that the hardness value increased up to 100g and the maximum hardness value was 46 kg/mm^2 at 100g.

According to Onitch [21], if the value of n is between 1 and 1.6, the material is hard and if it is greater than 1.6 the material is soft. Fig. 8 shows the plot of log P versus log d. The straight line in the graph shows its agreement with Meyer’s law. From the plot, the value of n is found to be 1.52. Hence UBC belongs to hard material category.

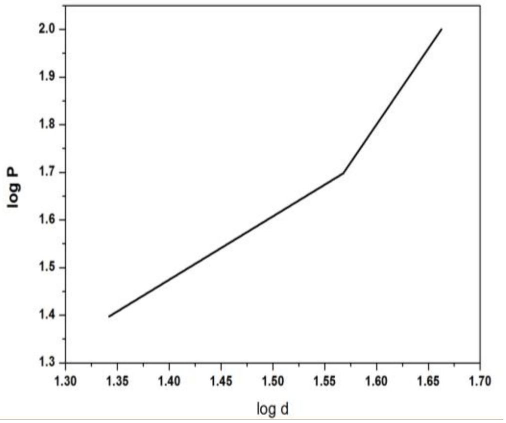

Fig. 8. Plot of log P (Vs.) log d for UBC crystal

3.8. Dielectric study

The dielectric characteristics of the material are essential to study the lattice dynamics in the crystal. Hence, the grown crystal was subjected to dielectric studies using 3532-50 HIOKI LCR meter. The variations of dielectric constant and dielectric loss against frequency at room temperature of the grown crystal are shown in Fig. 9 and 10. The dielectric constant (ε_r) was calculated using the relation, $\varepsilon_r = Cd/\varepsilon_0 A$, where C is the capacitance, d is the thickness of the crystal, ε_o is the vacuum dielectric constant and A is the area of the crystal. From the Fig. 9, it is observed that the dielectric constant is relatively higher in the initial region and further ε_r value decreases with increase in frequency. The high value of dielectric constant at low frequency is due to the presence of electronic, ionic, dipolar and space charge polarizations [22].

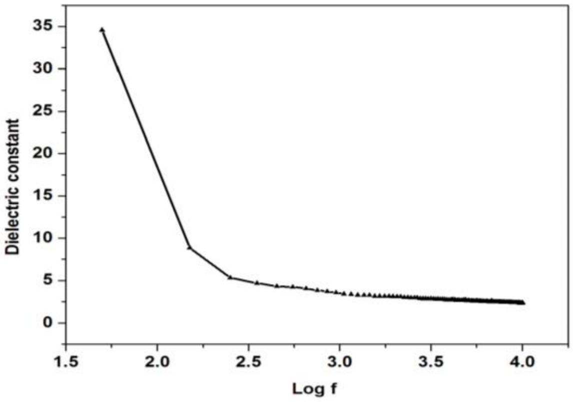

Fig. 9. Dielectric constant for UBC crystal

In accordance with Miller rule, the lower value of dielectric constant at higher frequencies is an appropriate parameter for the enhancement of second harmonic generation coefficient [23]. From Fig. 10, the characteristic of low dielectric loss with high frequency for the sample suggests that the crystal have enhanced optical quality with lesser defects which is the attractive property for NLO applications.

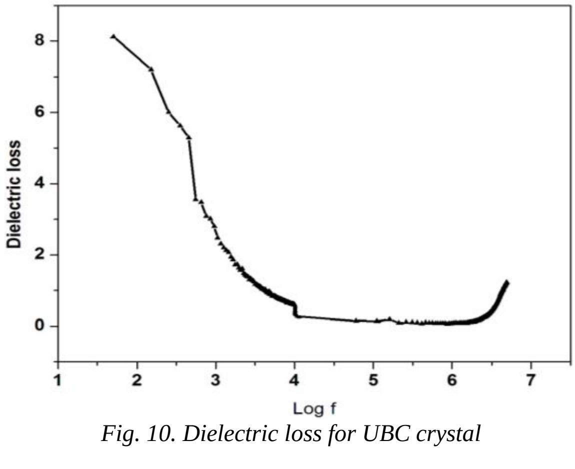

Fig. 10. Dielectric loss for UBC crystal

3.9. SHG test

The major broadly used technique for confirming the second harmonic generation (SHG) efficiency of NLO property to identify the materials with non-centrosymmetric crystal structures, is the Kurtz and Perry powder technique [24]. The primary beam of 1064 nm from Q-switched Nd:YAG laser is used to test the second harmonic generation (SHG) property of the UBC crystal. The input of pulse energy of 1.9±0.2 mJ pulse/second, pulse width of 8 ns and repetition rate of 10 Hz is used. For this measurement, the powdered form of KDP was used as a reference. The result of the present experiment shows that SHG conversion efficiency of KDP is 9 mV and the powder SHG efficiency of UBC is 7 mV. It is found to be near to KDP.

4. Conclusions

Good optical quality of NLO single crystals of urea barium chloride were effectively grown by slow evaporation technique. The EDAX analysis confirms the presence of elements. Powder X-ray diffraction confirms the crystallization nature. The lattice parameter is determined by single crystal X-ray diffraction analysis and the crystal belongs to monoclinic system. The sharp well defined Bragg’s peaks confirmed the crystalline nature. FTIR trace revealed the presence of amino groups and functional groups. The crystal has lower cut off wavelength at 320 nm and its transparency is calculated about 80%. The variations of dielectric properties were studied with varying frequency at room temperature. The NLO study was carried out and compared with KDP.

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References

[1] J. Ramajothi, S. Dhanuskodi, K. Nagarajan, Cryst. Res. Technol. **39**, 414 (2004).
[2] N. R. Dhumane, S. S. Hussaini, V. G. Dongre, P. Ghugare, M. D. Shirsat, Appl. Phys. A **95**, 727 (2009).
[3] K. C. Bright, T. H. Freeda, Appl. Phys. A **99,** 935 (2010).
[4] J. Chandrasekaran, P. Ilayabarathi, P. Maadeswaran, Opt. Commun. **285**, 3872 (2012).
[5] J. Chandrasekaran, P. Ilayabarathi, P. Maadeswaran, P. Mohamed Kutty, S. Pari, Opt. Commun. **285,** 2096 (2012).
[6] Redrothu Hanumantharao, S. Kalainathan, Spectrochim. Acta Part A, **86,** 80 (2012).
[7] L. Zeng M. Zha M. Ardoino P. Franzosi, L. Zanotti, G. Zuccalli, C. Paorici, J. Cryst. Growth, **166**, 528 (1996).
[8] S. E. Joema, S. Perumal, S. Ramalingam, P. Selvarajan, Rec. Res. Sci. Tech. **3**, 63 (2011).
[9] I. S. Prameela Kumari, C. K. Mahadevan, Int. J. Eng. Res. App. **3**, 1508 (2013).
[10] B. Sivasankari, P. Selvarajan, J. Exper. Sci. **1**, 1 (2010).
[11] Sweta Moitra, Tanusree Kar, Mater. Lett.**62**, 1609 (2008).
[12] G. Madhurambal, M. Mariappan, Asian J. Chem. **20**, 5067 (2008).
[13] J. T. Prakash, N. Vijayan, S. Kumararaman, Spectrochim Acta A Mol Biomol Spectrosc. **71,** 1250 (2008).
[14] M. Meena Kumari, C. Ravikumar, M. Amalanathan, V. S. Jayakumar, I. Hubert Joe, AIP Conf. Proc. **1075**, 101 (2008).
[15] S. Vetrivel, K. Kanagasabapathy, V. Praveenkumar, R. Arul jothi, Int. J. Lat. Tec. Eng. Appl. Sci. **3**, 10 (2014).
[16] V. Regina Delcy, V.S. John, S. Perumal, P. Selvarajan, Inter. J. Adv. Sci. Tech. **4**, 598 (2014).
[17] P. Malliga, C.A. Gonsago, R. Umamaheshwari, A. Joseph Arul Pragasam, Proc Indian Natn. Sci. Acad. **79,** 427 (2013).
[18] G. Madhurambal, M. Mariappan, Ind. J. Pure and Appl. Phy. **48,** 264 (2010).
[19] D. Gora, K. Parlinski, J. Chem. Phy. **113**, 8138 (2000).
[20] G. Madhurambal, M. Mariappan, Inter. J. Pharm. Chem. Sci. **2**, 1181 (2013).
[21] Onitsch E.M., Mikroscopia, **2**, 1947, 131.
[22] M.Vimalan, T. Rajesh Kumar, S. Tamilselvan, P. Sagayaraj, C. K. Mahadevan, Physica B, **405**, 3907 (2010).
[23] C. Justin Raj, S. Dinakaran, S. Krishnan, B. Milton Boaz, R. Robert, S. Jerome Das. Opt. Commun. **281**, 2285 (2008).
[24] S. K. Kurtz, T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).

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