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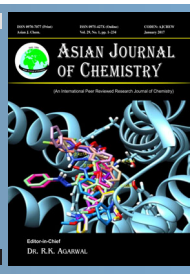

Synthesis, Structural, Optical, Thermal and LDT Characterization of Novel Semi-Organic Non-Linear Optical Material: Calcium Borolactate

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A new non-linear optical semi organic crystal calcium borolactate was developed by solution growth cum slow evaporation method. Single crystal XRD studies exposed that the calcium borolactate crystal accord to orthorhombic with the space group P_{212121}. The unit cell parameters are a = 8.49560(1) Å b = 10.0527(2) Å c = 21.3733(3) Å v = 1825.36(5) z = 4, 1.3469(1) mg m^{-3} R = 0.03 and Mr = 1181.08. The heading compound has also been characterized by UV-visible, FTIR, TGA/DSC studies. Non-linear optical studies shown that calcium borolactate exists a SHG coincide efficiency which is 1.5 times more of KDP.

Keywords: Calcium borolactate, X-ray diffraction structural studies, UV-visible, LDT studies, Non-linear optical.

INTRODUCTION

Non-linear optical (NLO) crystals are an advanced class of inorganic materials which are used for various applications including optical computing, data processing, colour display *etc*. [1,2]. The specialty of non-linear optical borate crystals lies in their ability to broaden the range of harmonic generation in UV-visible region [3,4]. Hence development of semi-organic non-linear optical borate crystals was pursued by many researchers. The calcium borolactate shows many unique properties. High damage during peak condition is an important property for design use of non-linear optical materials. Optical parametric amplification is an important method to generate short pulses in visible and near IR. Q-switching is a known technique used broadly in laboratories and industries [4-6]. Opto electronic fibres used in medical field that examine brain function and are having the ability to deliver drug in to the nervous system [7]. Semi organic non-linear optical materials show most of the excellent potential characteristics and hence studied extensively. In current analysis, we report growth of calcium borolactate crystals and its characterization by single crystal XRD, UV-visible, FTIR, TGA/DTA, LDT and non-linear optical studies.

EXPERIMENTAL

Synthesis and crystal growth of calcium borolactate: Calcium borolactate was synthesized as colourless crystals from calcium carbonate, boric acid and lactic acid in the ratio of 1:2:4. The calculated amount of boric acid and lactic acid were first dissolved in double distilled water and calcium carbonate was added slowly, mixed well and stirred for about 6 h *via* magnetic stirrer and evaporated to dryness. The temperature was maintained at 40 °C. To grow best quality of the single crystals, the synthesized compound was dissolved in a mixture of 1:1 ethanol-water solvent and allowed for slow evaporation. Single crystals of dimension 11 mm × 9 mm × 3 mm were grown in a period of 30 days. The grown crystals of calcium borolactate are given in Fig. 1.

Fig. 1. Grown crystal of calcium borolactate

RESULTS AND DISCUSSION

UV-visible spectral analysis: Optical property of the crystal can be analyzed by UV-visible spectrum. The instrument used in the analysis was lambda 25 spectrophotometer.

The wavelength measured from 190 to 500 nm. The speed and data interval maintained in the analysis is 120 nm/min and 1,0000 nm (Fig. 2).

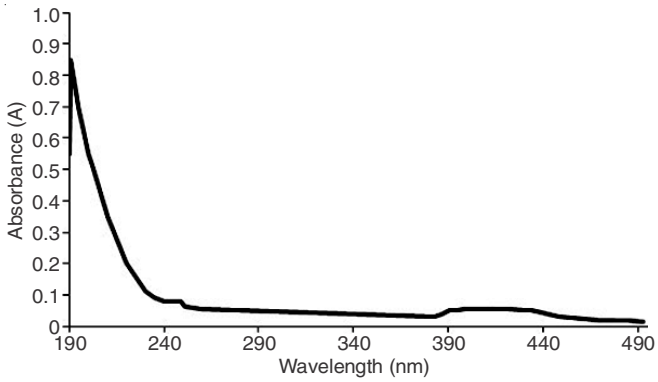

Fig. 2. UV-visible spectrum of calcium borolactate

Calcium borolactate shows incredibly low absorbance in the UV-visible region. The material exhibits ample transparency of about 83 % with a lower cut off wavelength of 230 nm. It's an another important property of the crystal for the manufacturing of optical devices. The band gap energy of calcium borolactate crystal was found to be 5.39 eV. As this crystal shows wide transmission range starting from 230 nm, it could to be used in optical devices.

FT-IR spectral studies: The FTIR spectrum was recorded with IFS Bruker instrument (66V spectrometer) and the spectrum shown in Fig. 3.

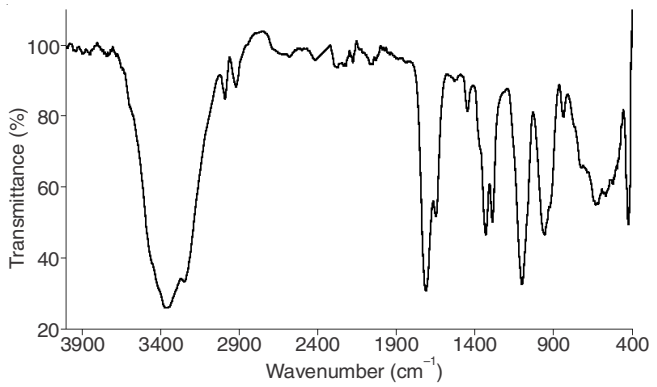

Fig. 3. FTIR spectrum of calcium borolactate

The frequency at 3370.96 cm^{-1} broad band indicates the presence of O-H stretching. The carbonyl stretching (C-O) is found to occur at 1713.44 cm^{-1} and indicates the occurrence of carboxylic acid group. The 1448.28 cm^{-1} peak shows the presence of C-O-H bonding. The peaks at 1331.61 cm^{-1} and 1101.15 cm^{-1} correspond to B-O asymmetric stretching vibrations. The B-O symmetric stretching vibrations arise at 956.52 and 836.955 cm^{-1}. Ca-O stretching vibration is confirmed from the peak at 632.537 cm^{-1}. All these assignments prove the existence of calcium and borate ions in the crystal lattice of lactic acid and are tabulated in Table-1.

TGA and DSC studies: Thermo gravimetric analysis and differential scanning calorimetry were performed to study the thermal stability of material. The analysis was carried out an instrument (SDT Q600 V20.9 Build 20) in N_2 atmosphere

TABLE-1
FUNDAMENTAL FREQUENCY OF VIBRATIONS OF CALCIUM BOROLACTATE CRYSTALS

Wavenumber (cm^{-1})	Assignment of functional group
3370.96	Stretching vibration of O–H
1713.44	Stretching vibration of C=O
1448.28	Bending vibration of C–O–H
1331.61	Asymmetric stretching vibration of B–O
1101.15	Asymmetric stretching vibration of B–O
956.52	Symmetric stretching vibration B–O
836.955	Symmetric stretching vibration B–O
632.537	Stretching vibrations of Ca–O

with a heating rate of 10 °C/min in the range of 36 to 1000 °C. 5.8330 mg of sample was used for crucible analysis. Fig. 4 shows that the calcium borolactate crystals are stable till 100 °C. The decomposition takes place in three stages. The initial decomposition begins at 100 °C and the weight loss could be attributed to the loss of three water molecules. This is closely followed by the second and third stages. The second decomposition at 200 °C and ends at 300 °C. The final decomposition occurs at 400 °C with the removal of 92.2 % sample in to gaseous products. The different gaseous products released are CO_2, OH and hydrocarbon gases. The unreacted mass of 7.80 % (0.4550 mg) which is remain in the crucible may be carbon. From the DSC graph, first endothermic peak at 100 °C indicates its melting point of calcium borolactate. Next endothermic peak at 300 °C is due to the elimination of the lactate ion and borate groups released from the compound respectively [8,9].

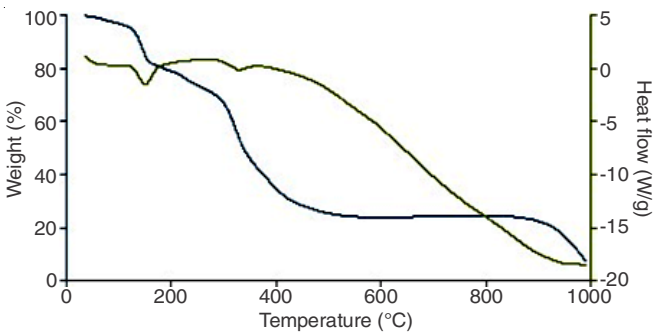

Fig. 4. TGA-DSC curve of calcium borolactate

Laser damage threshold studies: The potential of an optical crystal to resist very high densities of laser light is a key factor in various applications. The laser damage threshold value was measured using method Q switched high energy Nd:YAG laser (Quanta ray model lab-170-10) with pulse width (τ) of 6 ns and repetition rate of 10 Hz operating in TEM00 mode. The energy per pulse of 1064 nm laser radiation attenuated using appropriate neutral density filters was measured using an energy meter (EPM 2000, J-50-MB-YAG) which is externally triggered by Nd:YAG laser. For both single and multiple shots experiments, the sample was mounted on X–Y translator. For surface damage, the calcium borolactate crystal was placed at the focus of a plano-convex lens with focal length of 15 cm. The laser beam with diameter of 2 mm was focused on the crystal. An attenuator was used to vary the energy of the laser pulses with a polarizer and a half wave plate. The pulse energy of each shot was measured using the combination of a photo-

tube and an oscilloscope. The surface damage threshold of the crystal was calculated using the expression:

$$\text{Power density } (P_d) = E/\tau\ \pi r^2$$

where E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The measured laser damage threshold value of calcium borolactate is 14.92 GW/cm^2 for 1064 nm Nd:YAG laser radiation.

Non-linear optical test: The frequency doubling or second harmonic generation nature of calcium borolactate was examined using a Q-switched NdYAG laser by using Kurtz Perry powder technique. The frequency doubling nature of calcium borolactate is found to be 1.5 times higher than of KDP. Hence calcium borolactate is a potential materials which could be used in various photonic devices.

Single crystal structure analysis: Single crystal XRD data for calcium borolactate was collected at normal room temperature, using a Bruker Kappa diffractometer instrument with MoK$_\alpha$ radiation using ω/2θ scan mode. SMART APEX2 CCD area detector with MoK$_\alpha$ radiation and ω scan mode was used to acquire the exact unit cell parameters and matrix orientation within the least-square fit of numerous high angle reflections in the range $1.91° < \theta < 31.70°$. Cell fine-tuning and data reduction were carried out with SAINT [10]. A totality of 24175 reflections were collected, resulting in 6174 independent reflections of which 5360 had $I > 2\sigma(I)$. The intensities for lorentz and polarization effects and absorption corrections were changed by using SADABS [11]. The structure of compound was solved by direct method procedure as implemented in SHELXS97 [12,13] program. The full matrix least square refinement using SHELXL97 program was used to add the position of all non-hydrogen atoms. The thermal parameters for each atom were assigned a value of 0.05 (U's) in the initial stage and refinement was followed. The initial scale factor was pegged at 1.0. Thereafter the anisotropic refinement for a few cycles of full matrix least square was continued. At this stage the positions of all hydrogen's were geometrically fixed at calculated positions and they were allowed to ride on the corresponding non hydrogen atoms. The minimum and maximum value of residual electron density was -0.207, 0.238 e.Å^{-3} and the final R-factor were 0.0423. Crystallographic data of the compound is summarized in Table-2.

The ORTEP plot of calcium borolactate molecule drawn at 50 % probability ellipsoid level with atom numbering pattern shown in Figs. 5 and 6.

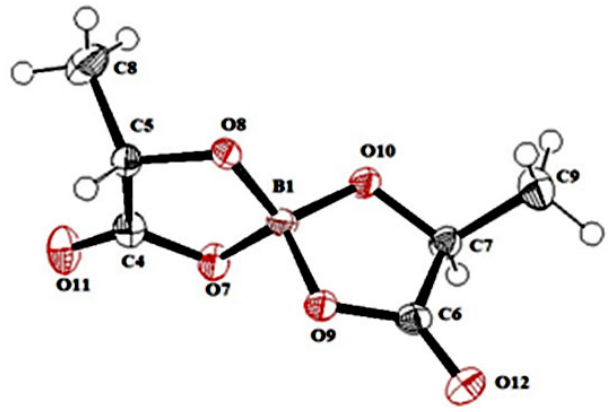

Fig. 5. ORTEP plot of calcium borolactate

TABLE-2
CRYSTAL DATA, DATA COLLECTION AND STRUCTURE REFINEMENT

Formula	$C_9H_{19}O_{12}BCa$
Formula weight	370.13
Crystal system	Orthorhombic
Space group	P212121
T (K)	295(2)
a (Å)	8.4956(1)
b (Å)	10.0527(2)
c (Å)	21.3733(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1825.36(5)
z	4
D_x (g cm^{-3})	1.347
F(000)	776
μ (mm^{-1})	0.395
Crystal size (mm)	0.32 × 0.25 × 0.14
θ range (°)	2.12–27.56
hkl range	$-12 \le h \le 10$; $-13 \le k \le 14$; $-31 \le l \le 31$
Reflections	
Collected	24175
Unique (R_{int})	6174 (0.0423)
With [$I > 2\sigma(I)$]	5360
Number of parameters	215
R(F) [$I > 2\sigma(I)$]	0.0423
wR(F^2) [$I > 2\sigma(I)$]	0.0684
R(F) [all data]	0.0331
wR(F^2) [all data]	0.0645
Goodness of fit	1.039
Max/min Δρ (e Å^{-3})	0.238/-0.207

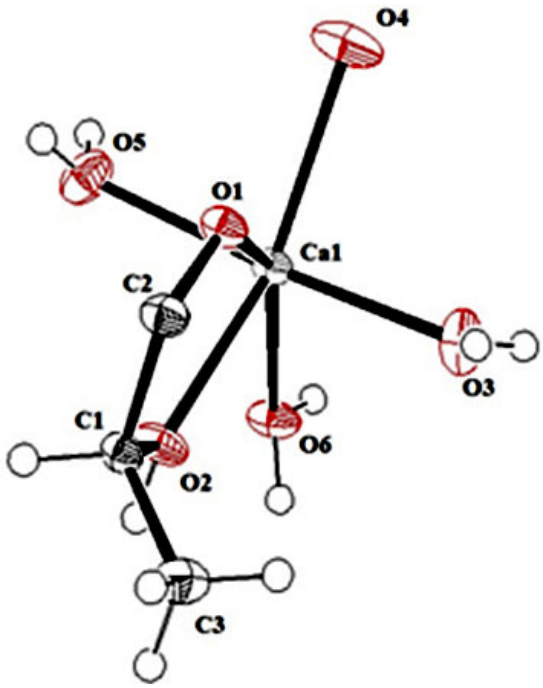

Fig. 6. ORTEP plot of calcium borolactate

The preferred geometrical parameters of the calcium borolactate summarized in Table-3.

The packing diagram of calcium borolactate is shown in Fig. 7.

TABLE-3
PREFERRED GEOMETRICAL PARAMETERS (Å)
WITH SU'S IN PARENTHESES

Preferred geometrical parameters (Å) with su's in parentheses		
Ca1 O6 2.3329(9)	O2 C1 1.4230(14)	O9 C6 1.3091(16)
Ca1 O3 2.3395(10)	O4 C2 1.2497(14)	O9 B1 1.5052(15)
Ca1 O1 2.3650(8)	C1 C3 1.5190(18)	O10 C7 1.4195(16)
Ca1 O2 2.3717(10)	C1 C2 1.5258(18)	O10 B1 1.4382(17)
Ca1 O5 2.3743(10)	C2 O4 1.2497(14)	O11 C4 1.2246(17)
Ca1 O4 2.4355(10)	C2 Ca1 2.8293(13)	O12 C6 1.2209(15)
Ca1 O1 2.5152(9)	O7 C4 1.3067(16)	C4 C5 1.5180(19)
Ca1 C2 2.8294(13)	O7 B1 1.5010(18)	C5 C8 1.5146(19)
Ca1 C2 3.2310(12)	O8 C5 1.4278(17)	C6 C7 1.5160(18)
O1 C2 1.2640(15)	O8 B1 1.4386(16)	C7 C9 1.518(2)
O1 Ca1 2.5152(9)		

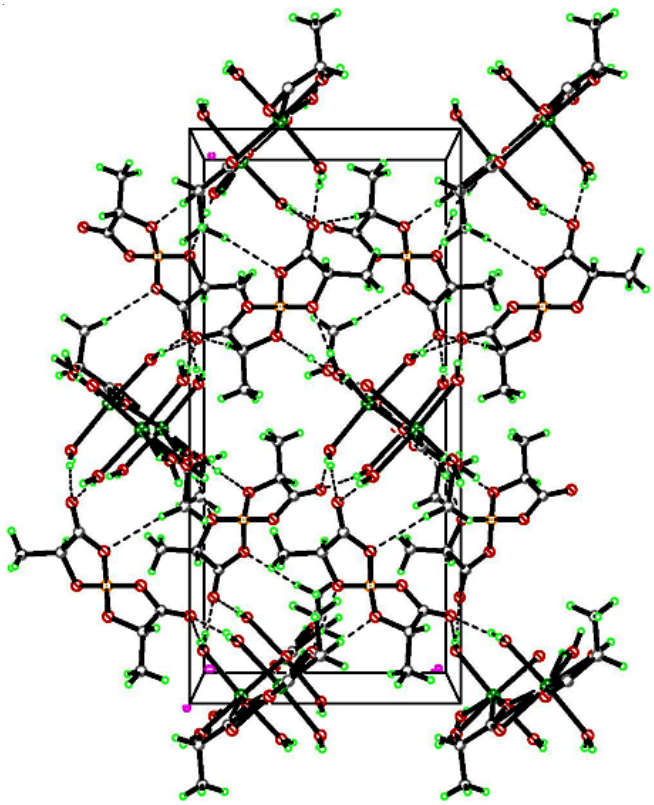

Fig. 7. Packing diagram of calcium borolactate

The molecular structure is stabilized by weak intra-molecular O-H…O interaction. The atoms O11 and O4 are acting as potent acceptor for O3-H103…O11 and O6-H106…O4, hydrogen bond in which atoms O3 and O6 respectively donates a proton. The hydrogen bond data of the compound given in Table-4.

TABLE-4
NON-BONDED INTERACTIONS AND
POSSIBLE HYDROGEN BONDS (Å, °)

D-H...A	D-H	H...A	D...A	DHA
O3-H1O3...O11	0.82	2.01	2.8105(14)	168
O6-H1O6...O4	0.82	1.84	2.6571(13)	178

Conclusion

A novel non-linear optical material, calcium borolactate has been synthesized and characterized by single crystal X-ray diffraction studies. The crystal exhibit ample transparancy of about 83 % with lower cut off wavelength 230 nm. Hence, it can be used in optical devices. The functional groups have been determined by FTIR analysis. Thermal stability of calcium borolactate has been evaluated by TGA/DSC. It is highly stable up to 100 °C. The measured laser damage threshold value of calcium borolactate is 14.92GW/cm^2 for 1064 nm Nd:YAG laser radiation. From non-linear optical analysis, show that the second-harmonic generation (SHG) conversion efficiency of calcium borolactate is 1.5 times more than that of potassium dihydrogen phosphate (KDP) crystals.

REFERENCES

1. H.S. Nalwa and S. Miyata, Nonlinear Optics Molecules and Polymers, CRC Press: New York (1997).
2. P.N. Prasad and D.J. Williams, Introduction to Nonlinear Optical Effects in organic Molecules and Polymers, John Wiley & Sons Inc.: New York, USA (1991).
3. K. Hussain and P. Kumbhakar, *Braz. J. Phys.*, **36(4a)**, 1281 (2006).
4. N. Vijayan, N. Balamurugan, R.R. Babu, R. Gopalakrishnan, P. Ramasamy and W.T.A. Harrison, *J. Cryst. Growth*, **267**, 218 (2004).
5. T.V. Anderson, Ph.D. Thesis, Application of Nonlinear Optics and Optical Fibres, University of Aarhus, Denmark (2006).
6. R.M. Kumar, D. Rajan Babu, D. Jayaraman, R. Jayavel and K. Kitamura, *J. Cryst. Growth*, **275**, 1935 (2005).
7. R.B. Ganesh, V. Kannan, K. Meera, N.P. Rajesh and P. Ramasamy, *J. Cryst. Growth*, **282**, 429 (2005).
8. P. Anikeeva, SPIE, International Society of Optics and Photonics (2015).
9. K.A. Nandekar, J.R. Dontulwar and W.B. Gurnule, *Rasayan J. Chem.*, **5**, 261 (2012).
10. R.A. Khatri, S.S.C. Chuang, Y. Soong and M.M. Gray, *Energy Fuels*, **20**, 1514 (2006).
11. SAINT-Bruker AXS Inc., Madison Wisconsin 53719, USA (1994-1996).
12. G.M. Sheldrick, SADABS, University of Gottingen, Germany (1996).
13. G.M. Sheldrick, SHELXS97 & SHELXL97, University of Gottingen, Germany (1997).