Synthesis and characterization of novel non-linear optical material $La_2BaB_{10}O_{19}$

[1]G. B. Harde,[2]G. G. Muley*

[1]Associate Professor,[2]Associate Professor and Head
[1]Department of Physics, Shri R. R. Lahoti Science College, Morshi, Maharashtra, India-444905
[1]Department of Physics, Sant Gadge Baba Amravati University, Amravati, Maharashtra, India-444602

Abstract: A novel nonlinear optical (NLO) polycrystalline material-lanthanum barium borate (LBB) has been synthesized by the solid-state reaction method. The differential thermal analysis shows the material melts at 898°C. The synthesized material exhibits monoclinic crystal structure with the space group C2, which has been confirmed from powder X-ray diffraction study. The second harmonic generation (SHG) in the powder sample was examined by using Nd:YAG laser with a fundamental wavelength of 1064 nm. The test confirms the SHG by the synthesized material. From the Fourier transform infrared analysis, BO_3 and BO_4 are the ionic groups exist in the materials which are responsible to produce NLO phenomenon in the prepare samples.

***Keywords*: Lanthanum barium borate, solid-state reaction method, second harmonic generation**

I. INTRODUCTION

Among all the present nonlinear optical (NLO) materials, the series of borate-based materials has attracted special interest because of their outstanding advantages for generating ultraviolet as well as blue and green lights. Well known few borate-based crystals-β-BaB_2O_4(BBO), LiB_3O_5(LBO), $CsLiB_6O_{10}$ (CLBO), $KBe_2BO_3F_2$ (KBBF), $K_2Al_2B_2O_7$(KAB), $K_3YB_6O_{12}$ (KYB), $La_2CaB_{10}O_{19}$ (LCB), $Y_2CaB_{10}O_{19}$ (YCB), [1,8] and other have high NLO coefficient, high transparency in the UV-visible range, moderate birefringence, and low walk-off angle, good mechanical, chemical and thermal stability. Among these crystals' LBO is employed extensively for the generation of green lasers by frequency doubling of Nd: YAG lasers. In addition to NLO applications, due to their molecular structure few borate crystals are attractive candidates as lasing materials for Nd and Yb. These crystals show self-frequency doubling (SFD) process. Researchers are getting the laser of different wavelength in the visible and ultraviolet region through second harmonic generation (SHG), third harmonic generation (THG), frequency mixing, optical parametric oscillations (OPO) etc with the help of NLO crystals. The practical setup for the purpose needs to have a laser which consist of cavity, lasing medium, exciting source, Q-switching arrangement etc and an assembly having NLO crystal outside cavity to convert the fundamental frequency of the laser to other frequencies. In this type of assembly, laser source and frequency converting assembly are required and they are separate. In this case, two crystal needed to be used viz: laser crystal and NLO crystal. It is possible to dope the NLO crystal by active lasing element directly and excite it by the diode laser or by flash lamp and it is possible to get directly second harmonic, third harmonic, sum frequency, difference frequency at the output. Thus, we need only to use only one crystal instead of using separate laser and NLO assembly.The examples of these kind of crystals are Yb:YCOB, Nd:GdCOB, Nd:YAB, and Yb:LCB [9-11].

Wu et al. have investigated firstly the lanthanum calcium borate (LCB) having chemical formula$La_2CaB_{10}O_{19}$ using La_2O_3-CaO-B_2O_3system [7]. Since, then researcher works on this material and grew single crystals in centimeter-size by the several methods. The LCB crystal exhibits good NLO properties, such as high transparency range, high laser damage, suitable hardness and chemical stability. Cao et al. [12] obtained similar NLO materials with all these characteristics by substituting element strontium for calcium in LCB. When an attempt was made to substitute strontium for calcium in LCB, a novel compound $La_2SrB_{10}O_{19}$was obtained which has high SHG efficiency than potassium dihydrogen phosphate KH_2PO_4 (KDP). Similarly, Kumar et al. [8] have prepared same kind of borate-based crystal by substituting yttrium for lanthanum in LCB and grown a new crystal yttrium calcium borate (YCB) with the chemical formula $Y_2CaB_{10}O_{19}$.The powder SHG efficiency was found in the grown crystal twice that of KDP. The laser induced damage was found of the order of 10.5 GW/cm^2. We followed same process to obtain similar NLO materials by substituting barium for calcium in LCB.

In the present attempt barium has been substitute for calcium in LCB to obtain a novel compound $La_2BaB_{10}O_{19}$ by solid-state reaction method. The synthesized compound has been characterized and studied its properties systematically. Powder XRD studies confirm the structure of the materials as the monoclinic crystal system with C2 space group. The FTIR study reveals the presence of BO_3 and BO_4 ionic groups which are suitable for NLO application. The DTA study confirms the melting point at 898°C. The NLO test confirms the SHG in the synthesized material.

II. MATERIAL SYNTHESIS

The high-temperature solid-state reaction method was used to synthesis polycrystalline samples of $La_2BaB_{10}O_{19}$. The raw materials used were La_2O_3 with purity of 99.99%, $BaCO_3$ and H_3BO_3 with analytical grade. All chemicals were purchased from Fisher Scientifics, Mumbai. The amounts of $BaCO_3$, La_2O_3, H_3BO_3 were weighted accurately according to the following stoichiometric chemical reaction:

$$La_2O_3+BaCO_3 +10H_3BO_3 \rightarrow La_2BaB_{10}O_{19} + CO_2 \uparrow +15H_2O \uparrow$$

During the solid-state reaction method 2 wt % excess amount of H_3BO_3 was added to compensate the evaporation of H_3BO_3. The mixture was heated at 500°C for 10 h, cooled and ground, and then heated again at 900 °C for12 h [13-15]. The polycrystalline powder of $La_2BaB_{10}O_{19}$ was obtained. The melting behavior of the synthesized$La_2BaB_{10}O_{19}$ was determined using a NETZCH STA 499C Simultaneous Thermal Analyzer. There are two apparent endothermic peaks in the DTA curveof$La_2BaB_{10}O_{19}$. It seems clear that $La_2BaB_{10}O_{19}$ melts incongruently and hence this crystal can be grown by flux method.

III. RESULTS AND DISCUSSION

3.1 Powder X-Ray Analysis of LBB

Synthesis samples of LBB material was subjected to X-ray powder diffraction (XRD) analysis, to study the structural and morphological characterization. The XRD pattern of sample has recorded and shown in the Fig. 1. The XRD peaks of the sample was indexed using software Powder X [16]. The XRD pattern of the synthesized powder sample was found to be nearly close to that of LCB there is little change in unit cell parameters. The unit cell parameters of LCB, which are a = 11.456Å, b = 6.340Å, c = 9.217Å and a=c =90º and b = 91.68º, were used as initial inputs to determine unit cell parameters of LBB [7]. The calculated unit cell parameters of LBB are a=10. 90215Å, b=6.55088Å, c=9.03041Å and α = γ =90°, β =92.21°. The LBB material belongs to the monoclinic crystal system with C2 space group.

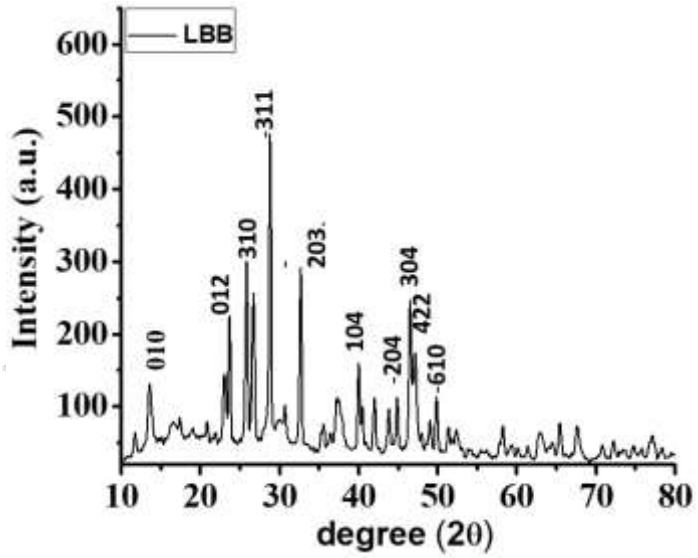

Fig.1: Powder XRD pattern of LBB material

3.2FT-IR Analysis of LBB

Fourier transform infrared (FTIR) analysis is a widely used to identify the functional groups present in material. This analysis helps to understand the nature of B–O network present in the materials. Well crushed polycrystalline powder sample of LBBwas mixed with KBr, pelletized and subjected to the FTIR) analysis between 4000 and 400 cm^{-1} in the transmittance mode at room temperature (Fig. 2). The vibrational bands of borate network are mainly observed in three spectral regions: 1500–1200 cm^{-1} (B–O stretching of trigonal BO_3 units), 1200–850 cm^{-1} (B–O stretching of tetrahedral BO_4 − units) and 800–600 cm^{-1} (bending vibrations of various borate segments) [17-25]. The strong band around 715 cm^{-1} is attributed to the vibration mode of $(B_3O_6)^{3-}$ ring and this result is closer to the reported peak at 775 cm^{-1} observed for BBO. This is considered to be one of the most important characteristic features. The intense broad band at 1467 cm^{-1} and those appearing below it are due to B–O and B–O–B bridge. This three-coordinated boron having a B–O–B linkage enhances the conjugation and probably leads to the electron delocalization. In the case of crystals like BBO and LBO, the observed large NLO activity is due to B-O bonding present in the crystal. The peaks in the range of 1000–1300 cm^{-1} are due to the asymmetric stretching of $(BO_3)^{3-}$ units. In number of borate crystals shows that the BO_4 tetrahedra produced the symmetric stretching vibration and asymmetric stretching vibrations. The peaks at 2261, 2376 and 2517 cm^{-1} are due to overtones and combination bands.

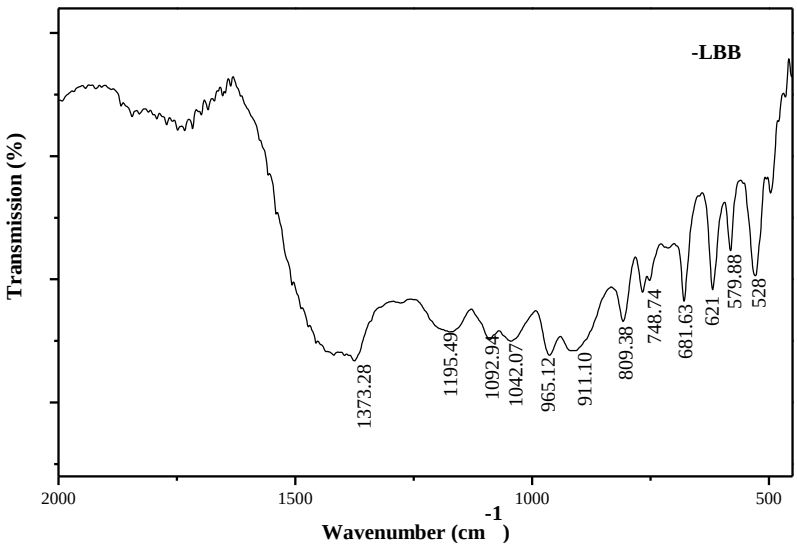

Fig.2: FTIR pattern of LBB material

Table 3.1: FT-IR peaks assignments of pure Nd and Yb doped LBB.

Peaks (cm^{-1})	Assignments
515	symmetric stretching motions in B–O–Ba bonds
581	
697	bending vibrations of various borate segments
763	
847	B–O stretching of tetrahedral BO_4^- units
973	
1164	B–O stretching of trigonal BO_3 units
1247	
1339	

3.3Differential thermal analysis of LBB

The synthesized polycrystalline powder of LBB sample was subjected to DTA to investigate melting temperature using a NETZSCH STA 449ºC simultaneous analyzer under static air. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated from room temperature to 1000ºC at a rate of 200 C/min. The DTA curve of LBB sample has shown in following figure. Pure LBB sample show two endothermic peaks at 624 and 898ºC on heating curve. The temperature corresponds to second peak well to the melting temperature, which has not reported in the literatures. Hence, this material has incongruent in nature and has phase transition below its melting point.

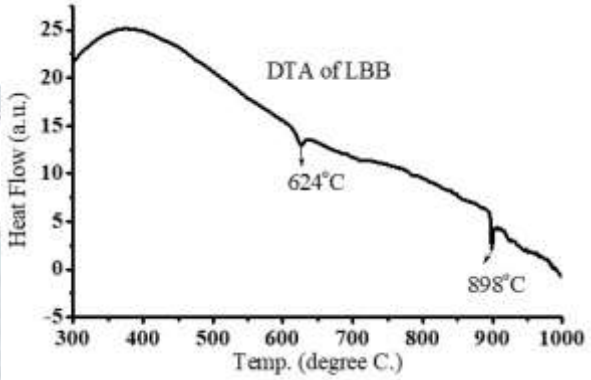

Fig.3: DTA curve of LBB powder sample

3.4Second Harmonic generation Study

In order to find out the NLO behavior of LBB material, SHG test was performed by the Kurtz and Perry powder technique [26] using Q-switched, mode locked Nd: YAG laser operating at the fundamental wavelength 1064 nm, generating around 6 mJ $pulse^{-1}$. The experimental set up used a mirror and 50/50 beam splitter, to generate a beam with pulse energy of 6 mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a sample holder [27, 28]. The light intensities emitted from LBB material and KDP, used as reference, are shown in figure 4. From figure it is observed that an intensity for LBB material is lesser than KDP.

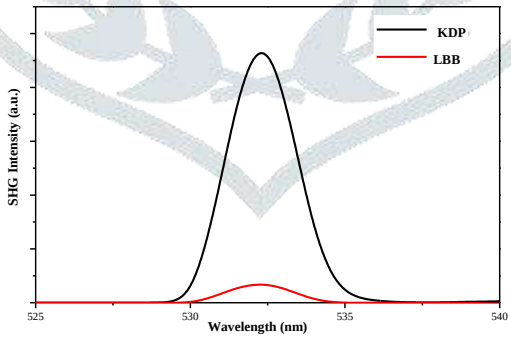

Fig. 4: Second harmonic generation curve of LBB powder sample

IV. CONCLUSIONS

In conclusion, a new mixed novel LBB borate material has been synthesized by solid-state reaction method. Powder XRD studies confirm the structure of the materials as the monoclinic crystal system with C2 space group. The FTIR study reveals the suitability of the materials for presence of BO_3 and BO_4 ionic groups for NLO application. The DTA study confirms the melting point for the LBB materials which have 898ºC. The NLO test is confirmed by Kurtz and Perry technique. The NLO test confirms the SHG by the synthesized material.

V.ACKNOWLEDGMENT

The authors GGM and GBH acknowledge financial support for this work from UGC, New Delhi under major research project (F. No. 41-925/2012 (SR)) and minor research project (F. No. 47-1363/10 (WRO)) respectively.

REFERENCES

[1] Kouta, H. Kuwano, Y. Ito, K. & Marumo, F. 1991. β-BaB_2O_4 single crystal growth by Czochralski method. II. Journal of crystal growth, 114(4): 676-682.

[2]Lin, S. Sun, Z. Wu, B. & Chen, C. 1990. The nonlinear optical characteristics of a LiB_3O_5 crystal. Journal of applied physics, 67(2): 634-638.

[3]Yap, Y. K. Haramura, S. Taguchi, A. Mori, Y. & Sasaki, T. 1998. $CsLiB_6O_{10}$ crystal for frequency doubling the Nd: YAG laser. Optics communications, 145(1-6): 101-104.

[4]Wu, B., Tang, D., Ye, N., & Chen, C. (1996). Linear and nonlinear optical properties of the $KBe_2BO_3F_2$ (KBBF) crystal. Optical Materials, 5(1-2), 105-109.

[5]Hu, Z. G. Higashiyama, T. Yoshimura, M. Yap, Y. K. Mori, Y. & Sasaki, T. 1998. A new nonlinear optical borate crystal $K_2Al_2B_2O_7$ (KAB). Japanese journal of applied physics, 37(10A): L1093.

[6]Zhao, S. Zhang, G. Yao, J. & Wu, Y. 2012. $K_3YB_6O_{12}$: A new nonlinear optical crystal with a short UV cutoff edge. Materials Research Bulletin, 47(11): 3810-3813.

[7]Wu, Y. Liu, J. Fu, P. Wang, J. Zhou H., Wang, G. & Chen, C. 2001. A new lanthanum and calcium borate $La_2CaB_{10}O_{19}$. Chemistry of materials, 13(3): 753-755.

[8] Arun Kumar, R. Arivanandhan, M. Dhanasekaran, R. & Hayakawa, Y. 2013. Growth and characterization of a novel nonlinear optical borate crystal – Yttrium calcium borate (YCB). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 110: 391–394.

[9]Hammons, D. A. Eichenholz, J. M. Ye, Q. Chai, B. H. T. Shah, L., Peale, R. E. &Qiu, H. 1998. Laser action in Yb^{3+}: YCOB (Yb^{3+}: $YCa_4O(BO_3)_3$). Optics communications, 156(4-6): 327-330.

[10]Schütz, I. Freitag, I. & Wallenstein, R. 1990. Miniature self-frequency-doubling cw Nd: YAB laser pumped by a diode-laser. Optics Communications, 77(2-3): 221-225.

[11]Guo, R. Wu, Y. Fu, P. & Jing, F. 2005. Growth and spectroscopic properties of ytterbium-doped lanthanum calcium borate (Yb^{3+}: $La_2CaB_{10}O_{19}$) crystal. Optics communications, 244(1-6): 321-325.

[12]Cao, J. Wang, J. Fu, P. Guo, F. Yang, Z. & Wu, Y. 2000. Synthesis and characterization of a novel non-linear optical material $La_2SrB_{10}O_{19}$. Progress in crystal growth and characterization of materials, 40(1-4): 97-101.

[13]Harde, G. B. and Muley G. G. 2017. Synthesis and characterization of pure and Nd-doped Bismuth Zinc Oxyborate ($Bi_2ZnOB_2O_6$), Materials Today: Proceedings, 4: 9496–9499.

[14]Dagdale, S. Pahurkar, V. Muley, G. 2016. High Temperature Crystal Growth: An Overview,Macromol. Symp. 362: 139-141.

[15]Dagdale, S. R. 2015. Synthesis and optical study novelNd^{3+}:$Na_2Mg_2ZnB_4O_{10}$ single, online international interdisciplinary research journal, 5:105-110.

[16]Dong, C. 1999. PowderX: Windows-95-based program for powder X-ray diffraction data processing. Journal of Applied Crystallography, 32(4): 838-838.

[17]Dagdale, S. R. and Muley, G. G. 2016. Synthesis and Characterization of a Novel Nonlinear Optical Material $Mg_2Na_2ZnB_4O_{10}$,Procedia Technology, 24: 682-688.

[18]Chen, C. T. Bai, L. Wang, Z. Z. & Li, R. K. 2006. Development of new NLO crystals for UV and IR applications. Journal of crystal growth, 292(2): 169-178.

[19]Zhang, D. Kong, Y. & Zhang, J. Y. 2000. Optical parametric properties of 532-nm-pumped beta-barium-borate near the infrared absorption edge. Optics communications, 184(5-6): 485-491.

[20]Mori, Y. Yap, Y. K. Kamimura, T. Yoshimura, M. & Sasaki, T. 2002. Recent development of nonlinear optical borate crystals for UV generation. Optical Materials, 19(1): 1-5.

[21]Ardelean, I. &Toderas, M. 2006. FTIR structural investigation of $3B_2O_3$-BaO glass matrix containing manganese ions. Journal of Optoelectronics and advanced materials, 8(3): 1118.

[22]Bhat, S. I. Rao, P. M. Upadyaya, V. &Nagaraja, H. S. 2002. Growth and characterization of a new nonlinear optical mixed borate crystal. Journal of crystal growth, 236(1-3): 318-322.

[23]Aka, G. Kahn-Harari, A. Mougel, F. Vivien, D. Salin, F. Coquelin, P. &Damelet, J. P. 1997. Linear-and nonlinear-optical properties of a new gadolinium calcium oxoborate crystal, $Ca_4GdO(BO_3)_3$. JOSA B, 14(9): 2238-2247.

[24]Prabha, K. Kumar, T. R. Du, S. F. Vimalan, M. Dayalan, A. &Sagayaraj, P. 2010. Growth and characterization of a new non-linear optical barium strontium borate (BSB) single crystal. Materials Chemistry and Physics, 121(1-2): 22-27.

[25]Prabha, K. Feng, B. Chen, H. Bhagavannarayana, G. &Sagayaraj, P. 2011. Growth and characterization of a new non-linear optical tris lead tris barium borate (TLTBB) single crystal. Materials Chemistry and Physics, 127(1-2): 79-84.

[26]Kurtz, S. K. & Perry, T. T. 1968. A powder technique for the evaluation of nonlinear optical materials. Journal of applied physics, 39(8): 3798-3813.

[27]Dagdale, S. R. Pahurkar, V. G. Muley, G. G. 2016. Synthesis and second harmonic generation study of Nd^{3+} doped lithium alumino-borate nonlinear optical material, Res. J. Chem. Sci. 6(9): 58-60.

[28]Dagdale, S. R. Muley, G. G. 2016. Synthesis and optical properties of polycrystalline$Li_2Al_2B_2O_7$ (LABO), AIP Conf. Proc. 1728: 020436-1-4.