Non-Linear Optical Study of pure and Nd doped Lanthanum Strontium Borate (La$_2$Sr B$_{10}$O$_{19}$)

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Abstract: *Pure and Nd doped La$_2$SrB$_{10}$O$_{19}$ compounds have been successfully synthesized from the La$_2$O$_3$-SrO-B$_2$O$_3$ system via a solid-state reaction. The powder X-ray diffraction data is reported and the XRD pattern of the pure and doped La$_2$SrB$_{10}$O$_{19}$ powder samples were found to be very close to that of Yttrium Calcium Borate (YCB)and crystallizes in the monoclinic system and belongs to the C2 space group. As powder samples were characterized by Kurtz-Perry method for SHG efficiency. It has been observed that all samples show SHG efficiency about twice that of KH$_2$PO$_4$ (KDP). FTIR analysis identified the existence of functional groups B$_3$O$_6$ in the present powder samples, Differential thermal analysis (DTA) results show that, pure and Nd doped La$_2$SrB$_{10}$O$_{19}$melts incongruently and the melting temperature of pure sample is about 983°C. These powder samples were also characterized by scanning electron microscopy (SEM) and SEM images revealed that the pure and Nd doped LSB powder samples possess the layer growth morphology. Energy dispersive x-ray (EDX) spectroscopy shows elements present in both powder samples for its crystal structure and surface morphology studies. The results are presented and discussed.*

Keywords: Pure and Nd dopedLa$_2$SrB$_{10}$O$_{19}$ polycrystalline sample, solid-state method, Second Harmonic Generation (SHG)

1. Introduction

The series of borate as an on linear optical (NLO) material has attracted special interest because of their outstanding advantages for generating ultraviolet as well as blue and green light [1]. NLO crystals having borate and oxyborate materials used for frequency conversion in laser systems as well as in NLO devices because of their high UV transparency and good chemical stability properties. In the past decade well known NLO crystals of borate series such as YAl$_3$ (BO$_3$)$_4$ (YAB) [2], GdAl$_3$ (BO$_3$)$_4$ (GAB) [3], LaCa$_4$O (BO$_3$)$_3$ (LCOB) [4] YCa$_4$O (BO$_3$)$_3$ (YCOB) [5], GdCa$_4$O (BO$_3$)$_3$ (GdCOB) [6] and Na$_3$La$_9$O$_3$ (BO$_3$)$_8$ (NLOB) [7] has attracted considerable interest because it exhibits a relatively large SHG *efficiency* and the single crystal is easily grown. In 1998, Wu et al [8] discovered series of mixed borates of rare-earth elements and calcium with the composition R$_2$CaB$_{10}$O$_{19}$ (RCB) (R: rare-earth element) from the R$_2$O$_3$-CaO-B$_2$O$_3$ ternary system. Later, in 2001, the first member of this series La$_2$CaB$_{10}$O$_{19}$ (LCB) grow and crystallizes in the monoclinic system and belongs to the C2 space group. The lattice parameters were measured to be a=11.043 (3) Å, b=6.563 (2) Å, c=9.129 Å, α=γ=90°, β=91.4°. The crystal structure contains B$_5$O$_{12}$ groups as the basic units which are linked together to form an infinite double layer by sharing O atoms with one another. The Lanthanum (La^{3+}) atoms are present in layers and the Calcium (Ca) atoms are situated between those layers. LCB crystal has easy to grow, have moderate hardness, possess good mechanical properties, non-hygroscopic, large NLO coefficient, high transparency ranges from ultraviolet (UV) to infrared range, and have high damage threshold. So LCB is a promising NLO crystal [9].
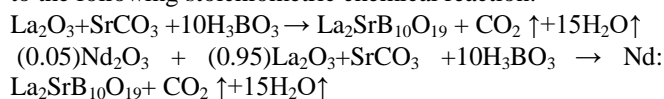
Considering above important properties of LCB crystals, Cao et al. (2000) synthesized similar NLO materials with all these characteristics by substituting elemental strontium, barium for calcium in LCB. When an attempt was made to substitute strontium for calcium in LCB, a novel compound La$_2$SrB$_{10}$O$_{19}$ was obtained for thefirst time [10]. But, as per the knowledge the single crystal growth of LSB has not been reported till date.

In this paper, we reported the synthesis of pure and Nd doped LSB materials by solid-state reaction method. The powder samples were characterized by different characteristic technique such as XRD analysis to study crystal structure, FTIR to identify the functional groups and differential thermal analysis (DTA) to know melting temperature. These powder samples were also characterized by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) the Kurtz-Perry method was used to study second harmonic generation (SHG) which confirmed that all samples show SHG about twice that of KH$_2$PO$_4$ (KDP). The data has been analysed and report has been presented.).

2. Material Synthesis

The high-temperature solid-state reaction technique was adapted to prepared polycrystalline samples of pure and doped La$_2$SrB$_{10}$O$_{19}$. The raw materials used were La$_2$O$_3$ with purity of 99.99%, SrCO$_3$ and H$_3$BO$_3$ with analytical grade. Neodymium Oxide (Nd$_2$O$_3$). All chemicals purchase from Fisher Scientics, Mumbai (India). The amounts of SrCO$_3$, La$_2$O$_3$ H$_3$BO$_3$andNd$_2$O$_3$ were weighted accurately according to the following stoichiometric chemical reaction:

La$_2$O$_3$+SrCO$_3$ +10H$_3$BO$_3$ → La$_2$SrB$_{10}$O$_{19}$ + CO$_2$ ↑+15H$_2$O↑
(0.05)Nd$_2$O$_3$ + (0.95)La$_2$O$_3$+SrCO$_3$ +10H$_3$BO$_3$ → Nd: La$_2$SrB$_{10}$O$_{19}$+ CO$_2$ ↑+15H$_2$O↑

During the solid-state reaction 2 wt% excess amount of H$_3$BO$_3$ was added to compensate for the evaporation of H$_3$BO$_3$. The mixture was heated at 500 °C for 10 h, cooled and ground, and then heated again at 1000°C for12 h. The polycrystalline powder of La$_2$SrB$_{10}$O$_{19}$ was obtained. Same method adopted for synthesis of Nd doped LSB. The melting behaviour of the synthesized samples were determined Differential Thermal Analyzer (DTA). The DTA curve of La$_2$SrB$_{10}$O$_{19}$ was recorded up to 1000 °C at a ramp rate of 20

°C/min. There are two apparent endothermic peaks in the DTA curve. It seems clear that sample melts incongruently and hence we can say that the crystal can be grown by the flux method.

3. Results and Discussion

3.1 Powder X-Ray Analysis of of pure and Nd doped LSB compound

The synthesised samples of pure and Nd doped LSB materials were subjected to X-ray powder diffraction (XRD) analysis, to study the structural and morphological characterization. The XRD spectra of both samples are recorded and shown in the Fig. 1. The XRD peaks of the samples were indexed using software Powder X [11].

The XRD pattern of the pure and doped powder samples were found to be very close to that of YCB, so we can deduce that there is no change isostructural in the presented pure and Nd doped compound as $La_2SrB_{10}O_{19}$. Furthermore,

we calculated the unit cell parameters of pure and doped $La_2SrB_{10}O_{19}$ by using those of YCB, which are a = 11.456 Å, b = 6.340Å, c = 9.217Å and α = γ =90° and β = 91.68°, as our basis [12]. The calculated values of lattice parameters as tabulated in table 1. and discuss with references, xrd pattern of YCB and LSB. The fact that the calculated XRD data of LSB coincide well with YCB. The synthesized compounds have the monoclinic crystal system with C2 space group.

Table 1: Unit cell parametrs of pure, Nd and Yb doped BZOB crystals.

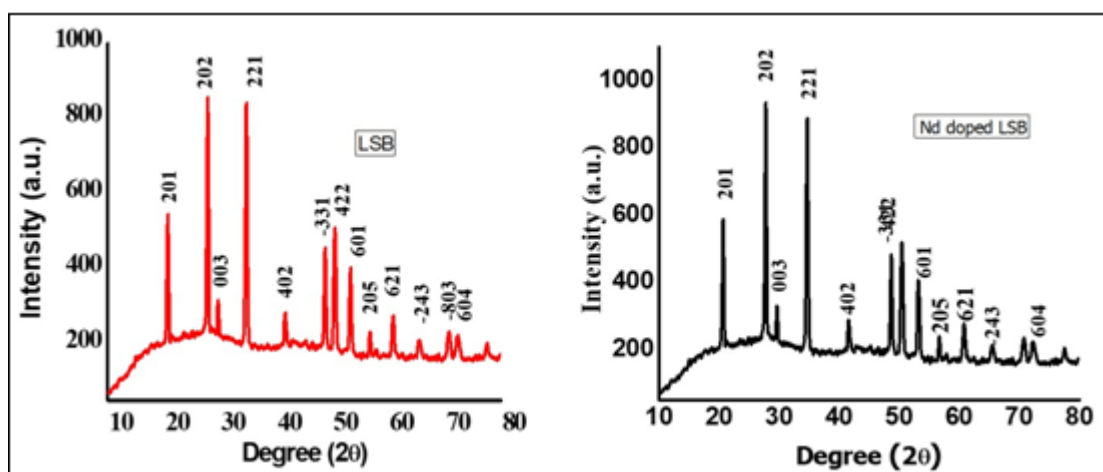|	LSB	Nd: LSB
Crystal system	monoclinic	monoclinic
Space group	C2	C2
a (Å)	10.985	10.984
b (Å)	6.570	6.586
c (Å)	9.116	9.049
α = γ (°)	90	90
β= (°)	91.76	91.84
Volume (Å³)	657.61	655.10

Figure 1: Powder XRD pattern of pure LSB and Nd doped LSB

3.2 FT-IR Analysis of pure and Nd doped LSB compound

Well crushed polycrystalline powder samples of pure and doped LSB were mixed with KBr, pelletized and subjected to the FTIR analysis in the frequency range 4000 and 400 cm⁻¹ in the transmittance mode at room temperature Fig.2. The vibration 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) [13-21]. 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 Barium Borate (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 [13]. This three-coordinated boron having a B-O-B linkage enhances the conjugation and probably leads to the electron delocalization [20]. 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 vibrations and asymmetric stretching vibrations [21]. The peaks at 2248, 2336 and 2517 cm⁻¹ are due to overtones and combination bands. Table 2 shows the peaks assignments of pure and Nd doped LSB.
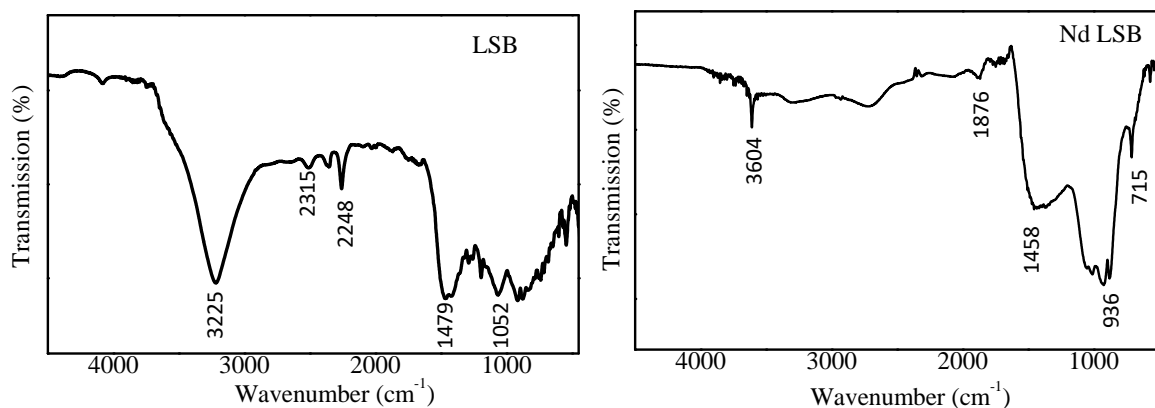
Figure 2: FTIR Spectra of pure LSB and Nd doped LSB

3.3 Differential thermal analysis of pure and Nd doped LSB compound

The melting behaviour of pure and Nd doped LSB samples were investigated by differential thermal analysis (DTA). The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated from room temperature to 1000° C at a rate of 20° C/min. The DTA curves of pure and doped LSB samples are shown in figure 3. Pure LSB sample show one endothermic peak at 983^oC on heating curve. The temperature corresponds to this peak well to the melting temperature, which has reported in the literatures [10]. It has no two endothermic peaks; however, it has reported as incongruent material. In case of Nd doped LSB samples, the DTA curve shows two endothermic peaks. For Nd doped LSB two peaks are at 947^oC and 979^oC. The temperature corresponds to the first peak indicate the phase change of material and second peak well to the melting temperature of sample [10]. Hence, these materials have incongruent in nature and has phase transition below its melting point. It has been observed that, melting temperature of doped materials decrease as compare to pure LSB sample.
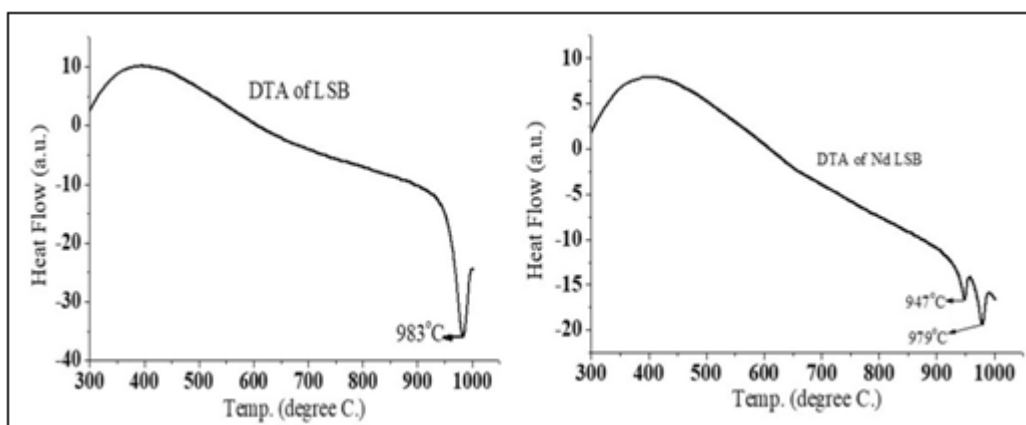

Figure 3: DTA curve of pure LSB and Nd doped LSB

3.4 EDX studies of pure and Nd doped LSB materials

As synthesised polycrystalline pure and Nd doped LSB materials has been crushed and ground into fine powder. These powder samples were subjected to EDX analysis. Fig 4. shows EDX spectra of pure LSB sample, 5 wt% Nd doped LSB sample respectively. Elements present in the both powder samples are thus observed from the spectra. The spectrum for pure LSB sample shows peaks only for La, Sr, B and O. Similarly, for Nd doped LSB, the peaks observed corresponding to energies for Nd, La, Sr, B and O are only observed. EDX analysis confirms the doping of Nd into LSB materials. Compositional information in terms of ratio of atomic weights from chemical formula are shown in table 2.

Table 2: Calculated compositional weights from Chemical formula and EDX analysis

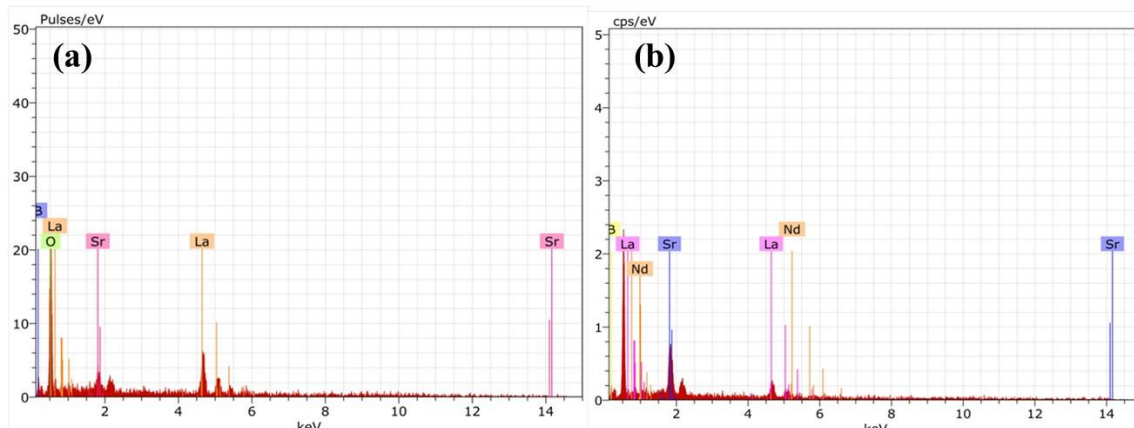| Element	Calculated atomic weight % from				% error	
	Chemical formula		EDX analysis			
	LSB pure	Nd: LSB	LSB pure	Nd: LSB	LSB pure	Nd: LSB
B	19.74	40.67	38.13	37.45	7.61	6.39
O	42.8	19.12	55.85	51.56	6.32	3.26
Sr	4.44	26.95	1.06	7.15	0.29	0.53
La	33.02	29.37	4.96	4.92	1.09	0.56
Nd		1.03		0.48		0.18
Total	100	100	100	100		

Figure 4: EDAX pattern of (a) pure LSB and (b) Nd doped LSB

3.5 Second Harmonic Generation Study of Pure and Nd doped LSB materials

In order to find out the NLO property of pure and Nd doped LSB materials, second harmonic efficiency 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 [27-32]. In the experimental set up a mirror and beam splitter were used to produce a beam with required pulse energy. The generate laser beam was passed through reflector and then strike on a capillary tube containing powdered sample. The light emitted by the sample was detected by and computer assembly. For the SHG efficiency measurements of KDP, a laser input of 6mJ was passed through Powder KDP sample which was used as the reference material and the powder SHG efficiency of materials decided from the intensity observed in figure 5. Intensity for Nd doped LSB materials greater than LSB as well as KDP. Hence, it is found that the SHG efficiency of the LSB sample is 2 times greater than that of KDP.
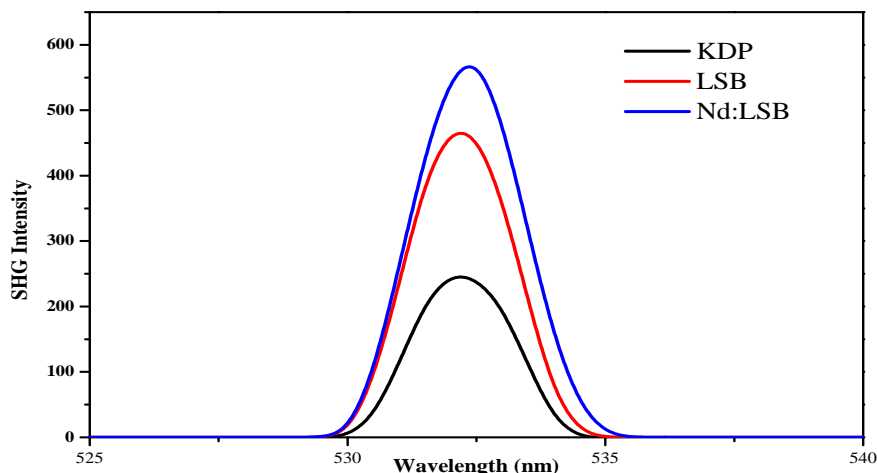

Figure 5: SHG intensity Plot of pure and Nd doped LSB

4. Conclusions

In conclusion, Pure and Nd doped $La_2SrB_{10}O_{19}$ (LSB) compounds have been synthesized from the La_2O_3-SrO-B_2O_3 system via a solid-state reaction. The powder XRD data is reported that the pure and doped LSB powder samples were found to be very close to that of Yttrium Calcium Borate (YCB) and crystallizes in monoclinic system and which is of the C2 space group. From SHG efficiency, it has been observed that all samples show SHG about twice that of KH_2PO_4 (KDP). The FTIR analysis identified the existence of functional group B_3O_6 in the present powder samples, Differential thermal analysis (DTA) results show that, pure and Nd doped LSB melts incongruently and the melting temperature for the pure and Nd doped LSB materials are 983^oC and 978^oC respectively. Energy dispersive x-ray (EDX) spectroscopy shows elements present in both powder samples for its crystal structure and surface morphology. Hence, LSB is a potential and attractive candidate for continued research and development as a NLO as well as Self frequency doubling (SFD) material.

Acknowledgment

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