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LOW TEMPERATURE SOLID-STATE SYNTHESIS AND CHARACTERIZATION OF $LaBO_3$

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Abstract: Rare earth (lanthanide series) borates, possess high vacuum ultraviolet (VUV) transparency, large electronic band gaps, chemical and environmental stability and exceptionally large optical damage thresholds. For this properties, they are used in the development of plasma display panels (PDPs). In this study the synthesis of lanthanum borates via solid-state method is studied. For this purpose, lanthanum oxide (La_2O_3) and boric acid (H_3BO_3) are used for as lanthanum and boron sources, respectively. Different elemental molar ratios of La to B (between 3:1 to 1:6 as La_2O_3:H_3BO_3) were reacted by solid-state method at the reaction temperatures between 500°C - 700°C with the constant reaction time of 4 h. Following the synthesis, characterizations of the synthesized products are conducted by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and scanning electron microscope (SEM). From the results of the experiments, three types of lanthanum borates of; La_3BO_6, $LaBO_3$ and $La(BO_2)_3$ were observed at different reaction parameters. Among these three types of lanthanum borates $LaBO_3$ phase were obtained as a major phase.

Keywords: lanthanide, borates, lanthanum borates, solid-state, XRD, SEM

Katı-Hal Yöntemi ile Düşük Sıcaklıklarda $LaBO_3$ üretimi ve Karakterizasyonu

Öz: Nadir toprak (Lantanit serisi) boratları, yüksek vakum ultraviyole şeffaflığına, büyük elektronik bant boşluğuna, kimyasal ve çevresel güvenilirliğe ve son derece geniş optik hasar eşiğine sahiptir. Bu özelliklerinden dolayı plazma ekran panellerinin geliştirilmesinde kullanılmaktadır. Bu çalışmada, katı-hal yöntemi ile lantan borat üretimi çalışılmıştır. Bu amaçla, lantan oksit (La_2O_3) ve borik asit (H_3BO_3) sırası ile lantan ve bor kaynağı olarak kullanılmıştır. Farklı elementel La ve B oranları (La_2O_3:H_3BO_3 olarak 3:1 den 1:6 ya kadar) katı-hal yöntemi ile 500°C - 700°C reaksiyon sıcaklıklarında, 4 saat süre ile reaksiyona sokulmuşlardır. Sentez sonrası ürünlerin karakterizasyonu X-ışınları difraktometresi (XRD), Fourier dönüşümlü kızıl ötesi spektroskopisi (FT-IR), Raman spektroskopisi ve taramalı electron mikroskobu (SEM) teknikleri ile gerçekleştirilmiştir. Deney sonuçlardan görüldüğü üzere, La_3BO_6, $LaBO_3$ ve $La(BO_2)_3$ yapısında üç farklı lantan borat bileşiği farklı parameterlerde saptanmıştır. Elde edilen farklı lantan borat bileşiklerinden $LaBO_3$ bileşiği major faz olarak elde edilmiştir.

Anahtar Kelimeler: lantanit, boratlar, lantan boratlar, katı-hal, XRD, SEM

1. INTRODUCTION

Highly concentrated, economically sized deposits of boron minerals always in the form of compounds with boron bounded oxygen which are rare and found in areas effected by volcanism or hydrothermal activity such as United States, Turkey and several other countries (Woods, 1994). Turkey and United States are dominating the production of boron compounds.

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Together they make up 90% of the world`s boron reserves (Harben and Kužvart, 1996). Total worldwide boron reserve is estimated to be 1.2 billion tons, where 72.2 % of these reserves are owned by Turkey (851 billion tons of B_2O_3) (T. R. Prime Ministry SPO (2006)).

Metal borates have various different types including the ones produced in with naturally existed ones. Metal borates produced in labs can be classified as monoborates and polyborates. Some of them has useful properties such as magnesium borates (Jun et al, 1997; Kıpçak, 2013).

There is an increasing attention to complex rare earth oxides and fluorides due to their practical significances. Perovskites, garnets, molybdates and borates of rare earth elements doped with atoms of other rare earth elements that have effective scintillation properties. Recently, particular attention has been paid especially for the extraordinary optical properties of these materials. Rare earth borates` high ultraviolet transparency, large electronic band gaps, chemical and environment stability and exceptional optical damage threshold make them optimum material for many practical applications such as gas discharge panels. Also Eu^{3+} doped yttrium and lanthanide orthoborates have proven to be potential candidates for new flat-panel display technologies (Badan et al., 2012; Lin, 2004).

Only a few studies about the synthesis of lanthanum borates were exits in the literature such as Shmyt'ko et al. (2013) studied the solid state reaction of $LaBO_3$ from amorphous precursors at high temperatures. Doi et al. (2013) studied the magnetic properties of lanthanide containing metal borates with 30% excess of H_3BO_3. In their study the mixture was pelletized and heated up to 1100°C (1°C/min) in a flow of N_2 gas. Rajaramakrishna et al. (2012) doped lead lanthanum borate with gold nanoparticles with the starting materials of La_2O_3, PbO, H_3BO_3 and $AuCl_3 \cdot HCl \cdot 4H_2O$. Lemanceau et al. (1999) investigated the domain of stability for lanthanum orthoborates using solid state reaction. The reactants were weighed, finely ground, and mixed. The mixture was then transferred in a platinum crucible and heated in a furnace. They stated that $LaBO_3$ below 750°C shows clearly the simultaneous presence of H-$LaBO_3$, $LaBO_3$, and La_2O_3 phases in the sample. Hu et al. (2000) synthesized nanoparticle lanthanum borate by hydrothermal method with a particle size of 20-40 nm but lanthanum borate which they produced, had an amorphous structure. They suggested that this material could be useful as anti-abrasion and anti-wear additives in oil or grease. Badan et al. (2012) synthesized lanthanum borate with microwave assisted combustion method and microwave assisted sol-gel method. In microwave assisted combustion method, he used 10 minutes of microwave heating and 2 hours of conventional furnace heating at 950°C and in microwave assisted sol-gel method reactants mixed with water at 80°C until they got in a gel phase then 10 minutes of microwave heating and 2 hours of conventional furnace heating at 950°C were applied. Ma and Wu (2007) synthesized $LaBO_3$ nanorods at 200°C temperature in 24 hours by a novel method named oxide-hydrothermal method.

Although solid-state reaction method is the most applicable method for lanthanum borate synthesis, reaching to high temperatures leads the energy inefficiency. In this study, it is aimed to synthesize lanthanum borates by solid-state method using the temperatures lower than the literature and determinate the optimum molar ratio of reactants. After the synthesis the characterizations of the products are conducted by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and scanning electron microscope (SEM). Also the reaction efficiencies are calculated.

2. EXPERIMENTAL METHOD

2.1. Preparation and Characterization of the Reactants

Lanthanum (III) oxide (La_2O_3) was supplied from Alfa Aesar (Alfa Aesar, Lancashire, UK) as a grade of REacton® (99.9% pure), which have a CAS Number of "1312-81-8" and used without any pretreatment. Boric acid (H_3BO_3) was obtained from Bandırma Boron Works (Eti Maden, Balıkesir, Turkey). $H_3BO_3$was treated by crushing, grinding and sieving processes to

obtain the particle size below 75μm. To identify the raw materials, PANalytical Xpert Pro (PANalytical B.V., Almelo, The Netherlands) XRD was used with the parameters of 45 kV and 40mA (Cu- Kα tube, λ=0.153 nm) and patterns were obtained at the range between 15-85°.

2.2. Solid State Synthesis and Characterizations of the Products

In the syntheses, different elemental molar ratios of La:B (La_2O_3:H_3BO_3) which ranged from 3:1 to 1:6 are mixed homogenously and pelletized with using Manfredi OL 57 model hydraulic press (Manfredi S.r.l., Torino, Italy). In the pelletization process, the samples are pressed at a pressure of 100 bars for the duration of two minutes. After the pelletization processes, the pellets are subjected in Protherm MOS 180/4 model high temperature furnace (Alser Teknik, Ankara, Turkey) by using the ceramic crucibles. The temperature increment is selected as 10°C/min, the reaction temperature and the reaction time are selected between 500°C – 700°C and 4 h, respectively. The expected reaction schemes are given through (1) to (3), where the theoretical elemental molar ratios are 3:1, 1:2 and 1:5 for the reactions of (1), (2) and (3), respectively.

$$3La_2O_3 + 2H_3BO_3 \Rightarrow 2La_3BO_6 + 3H_2O \quad (1)$$

$$La_2O_3 + 4H_3BO_3 \Rightarrow 2LaBO_3 + B_2O_3 + 6H_2O \quad (2)$$

$$La_2O_3 + 10H_3BO_3 \Rightarrow 2La(BO_2)_3 + 2B_2O_3 + 15H_2O \quad (3)$$

The same parameters of used in the part of "Characterization of the Reactants" are used in the XRD analysis except the range of pattern is recorded between 10-75°, since the characteristic peaks of lanthanum borates are found in that range. In Fourier transform infrared spectroscopy analysis, PerkinElmer Spectrum One FT-IR (PerkinElmer, MA, USA) is used with the parameters of 4 and 4 cm^{-1} as scan number and resolution, respectively. The spectrum range is recorded between 1800 – 650 cm^{-1}. Similarly, in Raman spectroscopy analysis, Perkin Elmer Raman Station 400F (PerkinElmer, CT, USA) is used with scan number of 4, scan time of 4 seconds and the spectrum range is recorded between 2000 – 250 cm^{-1}. In the SEM analyses, CamScan Apollo 300 Field-Emission SEM (CamScan, Oxford, United Kingdom) was used at 15kV with backscattering electron detector (BEI) and the magnification of the products was set to 10000 times.

2.3. Reaction Efficiencies

The reaction yields were calculated using (4) (Fogler, 1999):

$$Y_D = \frac{N_D}{N_{A0} - N_A} \quad (4)$$

where the overall yield (Y_D), is defined as the ratio of moles of product formed at the end of the reaction (N_D), to the number of moles of the key reactant (La_2O_3), that have been consumed. N_{A0} and N_A are the initial and final moles of consumed reactant, respectively.

3. RESULTS AND DISCUSSION

3.1. Raw Material Characterization Results

The XRD results of H_3BO_3 and La_2O_3 are found as "Sassolite (H_3BO_3)" with powder diffraction file number of (pdf no.) "01-073-2158" and "Lanthanum Oxide (La_2O_3)" with pdf no. of "01-073-2141".

3.2. Characterization Results of Produced Lanthanum Borates

3.2.1. XRD Results

XRD results of the synthesized lanthanum borates are given in Table 1. According to the Table 1, it is seen that three different types of lanthanum borates are obtained. These are coded as "LB^1" for La_3BO_6 (pdf no: 00-050-1379), "LB^2" for $LaBO_3$ (pdf no: 00-012-0762) and "LB^3" for $La(BO_2)_3$ (pdf no: 00-023-1140). Along with these lanthanum borates at some parameters the unreacted La_2O_3 (pdf no: 01-073-2141) is seen, which is coded as "L".

Table 1. XRD results of the synthesized lanthanum borates

Temperature (°C)	Molar Ratio	3:1	2:1	1:1	1:2	1:3	1:4	1:5	1:6
	Products	XRD Scores							
700	L	68	69	57	-	-	-	-	-
	LB^1	14	15	14	-	-	-	-	-
	LB^2	30	36	60	61	56	50	56	47
	LB^3	19	16	-	-	-	-	-	-
600	L	60	55	70	72	68	68	65	58
	LB^1	16	20	24	14	11	14	13	10
	LB^2	33	35	34	33	29	33	39	31
	LB^3	26	27	29	16	-	-	-	-
500	L	87	92	89	80	85	81	80	60
	LB^1	11	12	13	-	12	-	13	16
	LB^2	-	-	-	-	-	-	-	-
	LB^3	15	-	-	-	-	-	-	-

At 500°C reaction temperature the major phase of "L" is seen with very high XRD scores (when all of the peak intensities (%) and peak locations are matched perfectly with the pdf card no of reference mineral, the XRD score of analyzed mineral is equal to 100) at all of the molar ratios meaning that nearly all of the "L" was remain unreacted in the system. Also in 500°C reaction temperature at some molar ratios "LB^1" phase is obtained with very small XRD scores, so it can be said that the "LB^1" formation was started with 500 °C reaction time. At 600°C, unreacted "L" phase is also seen but the XRD scores are decreased compared to 500°C reaction temperature. Also the phases of "LB^1", "LB^2" and "LB^3" are seen together at the molar ratios between 3:1 to 1:2. At the ratios between 1:3 to 1:6, LB^1" and "LB^2" phases are seen. Among obtained lanthanum borates "LB^2" phase is obtained as major phase and the highest XRD score of 39 is seen at the molar ratio of 1:5.

When the reaction temperature is increased to 700°C, only the unreacted "L" is seen at the ratios between 3:1 to 1:1, where the elemental molar ratio of La is higher or equal to B ratio. After the molar of 1:1 "L" phase is not seen meaning that all of the "L" phase is reacted with

H_3BO_3 and turned to lanthanum borates. Among the lanthanum borate phases "LB^{1}" phase is seen only the molar ratios between 3:1 to 1:1 and "LB^{3}" phase is seen only the molar ratios of 3:1 and 2:1. The major phase of "LB^{2}" is seen at all of the molar ratios, and obtained as a pure phase at the molar ratios between 1:2 to 1:6 with the XRD scores between 47 – 61. The highest XRD score of 61 is obtained in the molar ratio of 1:2. The pure "LB^{2}" phases XRD patterns are given in Figure 1.

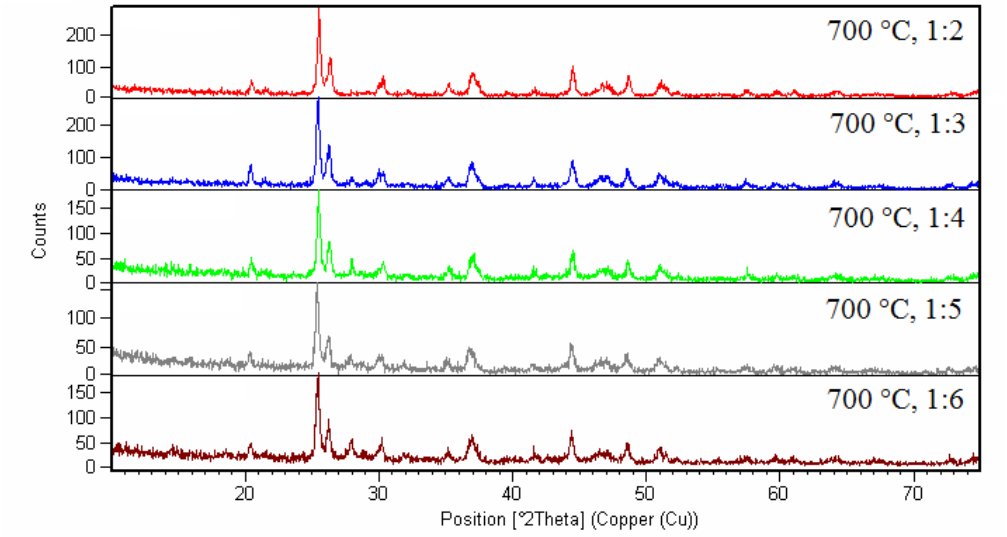


Figure 1:
XRD patterns of pure "LB^{2}" phases

According to the Figure 1, the characteristic peaks of $LaBO_3$ is seen at the 2θ degree of 20.45°, 25.49°, 26.37°, 30.42°, 35.12°, 36.92°, 37.06°, 44.44° and 48.68°. The crystallographic data of $LaBO_3$ is given in Table 2.

Table 2. $LaBO_3$ crystallographic data

Mineral Name (Chemical Formula)	Lanthanum borate ($LaBO_3$)
Pdf No.	00-012-0762
Molecular weight (g/mol)	197.7147
Crystal System	Orthorhombic
Space Group (No)	Pnam (62)
a (Å), b (Å), c (Å)	5.8720, 8.2570, 5.1070
α (°), β (°), γ (°)	90.00, 90.00, 90.00
z	4
Density (calculated) ($g.cm^{-3}$)	5.30

3.2.2. FT-IR and Raman Results

FT-IR and Raman peak results and spectra of the pure "LB^2" phases are given in Table 3, Figure 2 and Figure 3, respectively.

From FT-IR results and the spectra 4 different peak regions are observed at around 1267-1266 cm^{-1}, 1194-1193 cm^{-1}, 939-938 cm^{-1}, 881-880 cm^{-1} and 707-698 cm^{-1}. These bands can be described as asymmetrical stretching of four coordinate boron to oxygen [$\nu_{as}(B_{(4)}\text{-}O)$], bending of boron-oxygen-hydrogen [δ(B-O-H)], symmetrical stretching of three coordinate boron to oxygen [$\nu_s(B_{(3)}\text{-}O)$] and symmetrical stretching of four coordinate boron to oxygen [$\nu_s(B_{(4)}\text{-}O)$].

Table 3. FT-IR and Raman Peaks

FT-IR Peaks (cm^{-1})	Peak Interpretation	Raman Peaks (cm^{-1})	Peak Interpretation
1267-1266	$\nu_{as}(B_{(4)}\text{-}O)$	1355-1290	$\nu_{as}(B_{(3)}\text{-}O)$
1194-1193	δ(B-O-H)	1223-1220	δ(B-O-H)
939-880	$\nu_s(B_{(3)}\text{-}O)$	942-940	$\nu_s(B_{(3)}\text{-}O)$
707-698	$\nu_s(B_{(4)}\text{-}O)$		

From Raman results 3 different peak regions are observed at around 1355-1290 cm^{-1}, 1223-1220 cm^{-1} and 942-940 cm^{-1}, which these bands are $\nu_{as}(B_{(3)}\text{-}O)$, δ(B-O-H) and $\nu_s(B_{(3)}\text{-}O)$.

These boron oxygen bands are in compatible with the studies in the literature (Yongzhong et al., 2000; Derun et al., 2015; Kipcak et al., 2014a; Kipcak et al., 2014b).

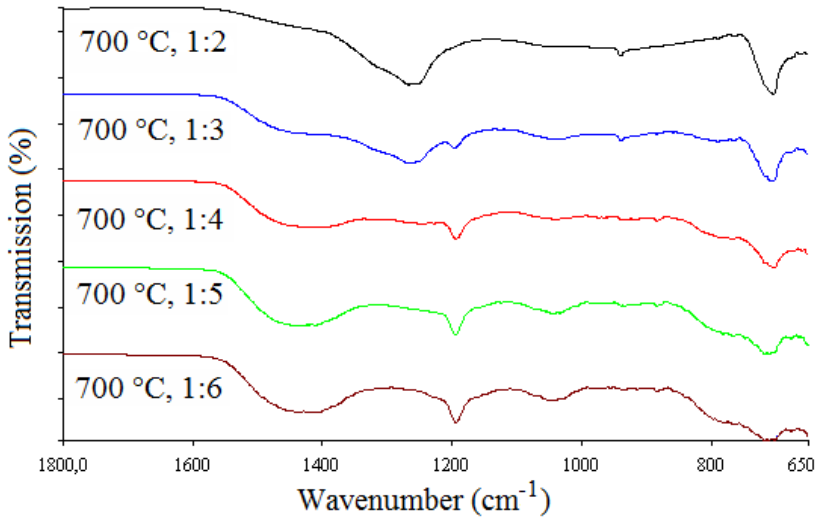


Figure 2:
FT-IR spectra of pure "LB^2" phases

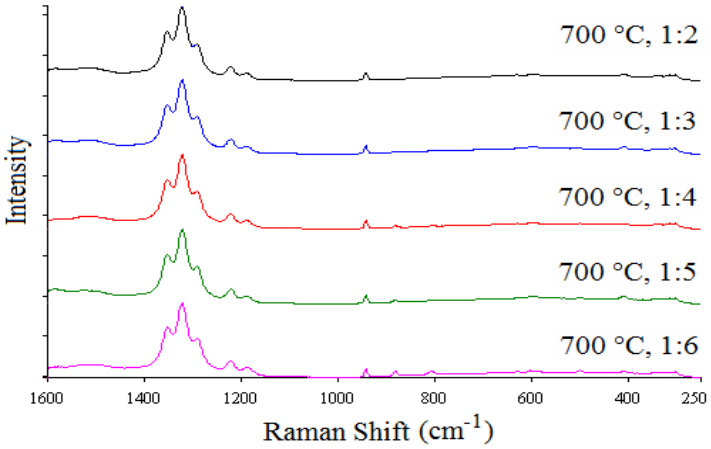
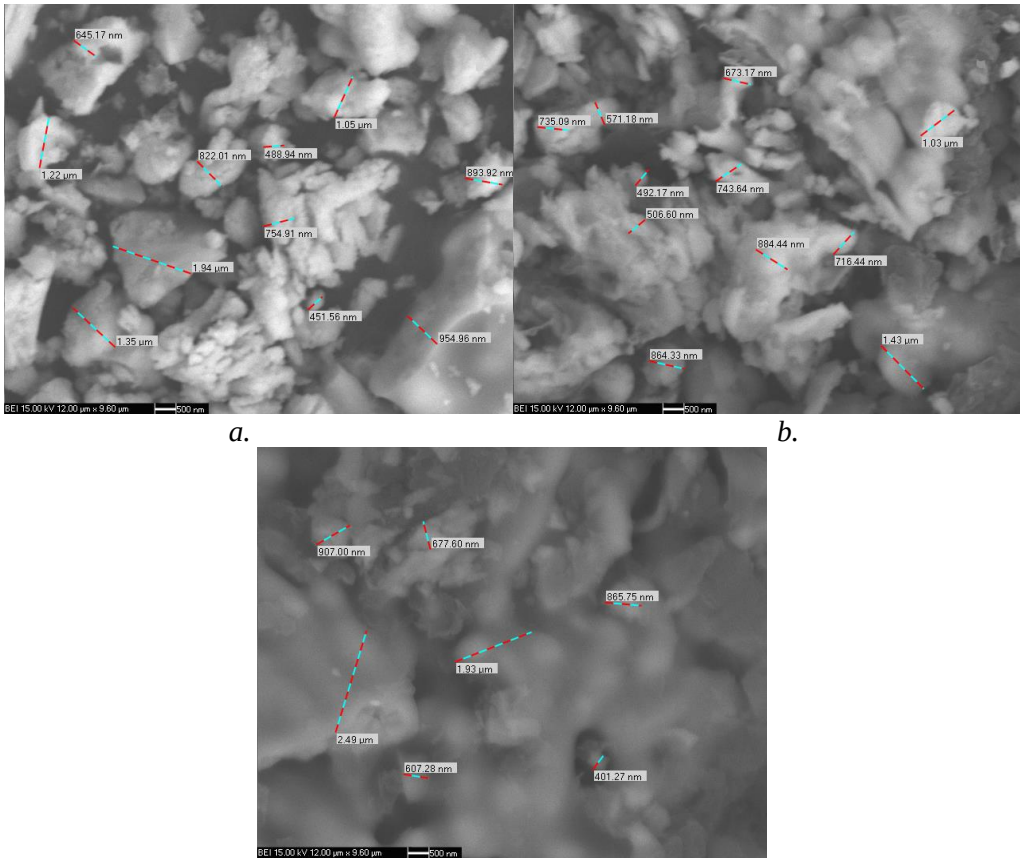


Figure 3:
Raman spectra of pure "LB^2" phases

3.2.3. SEM Morphologies

SEM morphologies and the particle sizes of the produced $LaBO_3$ with ratios 1:2, 1:3 and 1:4 molar ratios are given in Figure 4.



a. *b.*

c.

Figure 4:
SEM morphologies of
a. *1:2 molar ratio* ***b.*** *1:3 molar ratio* ***c.*** *1:4 molar ratio*

At 1:2 molar ratio, tubular type of crystals are found with some triangular type of crystals. Some agglomerations are also occurred and the particle sizes are found between 1.94 μm and 451.56 nm. At 1:3 molar ratio produced $LaBO_3$ crystals are partly rectangular and partly cylindrical. Also agglomerated particles are seen and the particles sizes are found between 1.43 μm and 492.17 nm. At the other molar ratio of 1:4, it is observed that the crystals are agglomerated and the morphology seems blurry. The particle sizes are found between 2.49 μm and 401.27 nm. From ratio of 1:2 to 1:3 the maximum particle sizes are decreased and minimum particle sizes are increased. From ratio of 1:3 to 1:4 the maximum particle sizes are increased and minimum particle sizes are decreased.

3.2.4. Reaction Efficiency Results

Three parallel experiments are conducted and the average of reaction efficiencies of pure "LB^2" phases are given along with standard deviations in Figure 5. According to the Figure 5, the reaction efficiencies are seen between 76.60 – 84.20 %. As it is expected from the theoretical reaction scheme of (2), where elemental molar ratio is 1:2., the highest reaction yield is achieved as 84.20 ± 0.55 %. At the other molar ratios through 1:3 to 1:6, the mixtures contain excess H_3BO_3, which leads a decrease in the reaction yields. The lowest reaction yield of 76.60 ± 0.42 % is found at the molar ratio of 1:6.

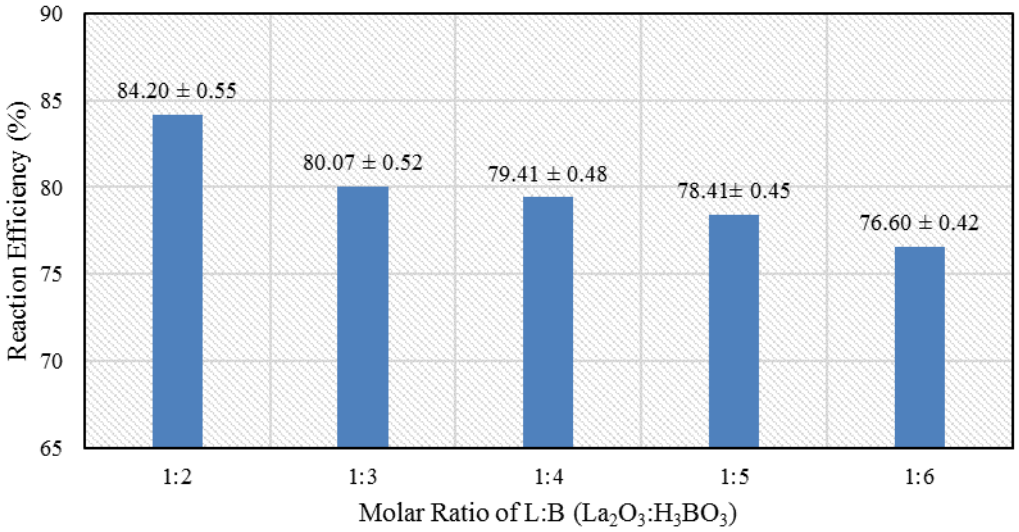


Figure 5:
Reaction efficiencies of pure "LB^2" phases

4. CONCLUSIONS

In this study the solid-state pure synthesis of $LaBO_3$ is achieved at the temperature of 700°C with the reactants of La_2O_3 and H_3BO_3. The optimum molar ratio of La_2O_3 to H_3BO_3 is found as 1:2, which its XRD score and reaction efficiency is found as 61 and 84.20 ± 0.55 %, respectively. Along with the ratio of 1:2, at the molar ratios between 1:3 to 1:6 pure formations of $LaBO_3$ phases are also seen. Obtained pure $LaBO_3$ phases FT-IR and Raman spectra results showed that the products contain symmetrical and asymmetrical stretching of three and four coordinate boron to oxygen bands, which these bands are the characteristic bands of boron minerals. The particle sizes of the synthesized $LaBO_3$ phases are found between 2.49 μm - 401.27 nm, where the particle size of the 1:2 molar ratio is found between 1.94 μm – 451.56 nm.

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