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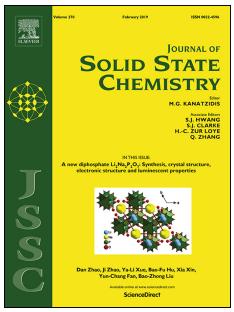

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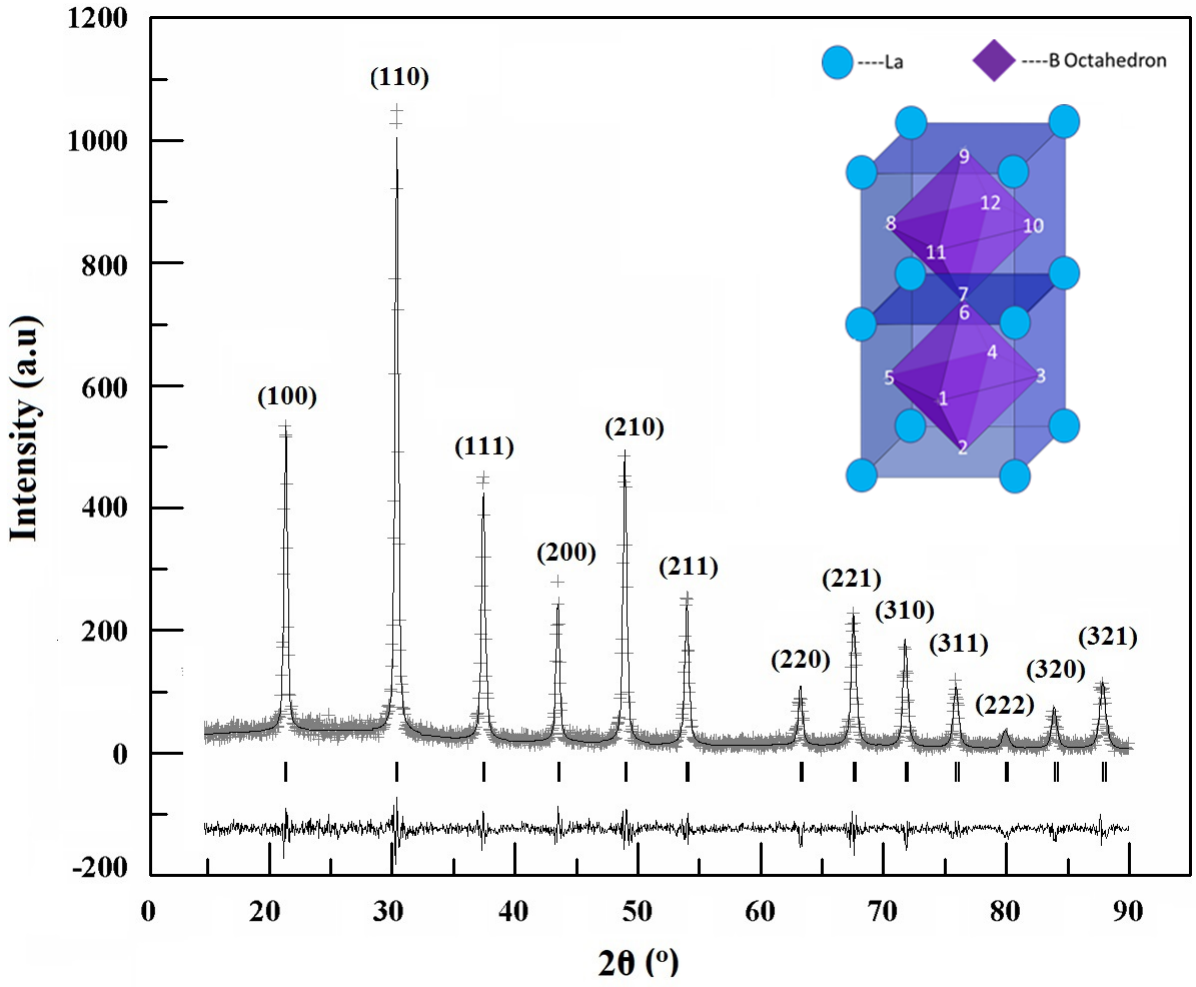

Low Temperature Synthesis and Characterization of Pure Lanthanum Hexaboride Nanocrystals

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Abstract:

This study aims to synthesize very pure form of LaB_6 nanocrystals at low temperatures. The synthetic route employed involved low temperature magnesiothermic reduction process of La_2O_3 with a mixture of Mg, I_2 and B_2O_3 at 90 □C. The powder mixtures were mechanically induced under Ar atmosphere for 3 hours and then heat treated. The pure form of nano LaB_6 powder produced by this technic is by far the most versatile route for the synthesis of nano-LaB_6. From the XRD evidences of the synthesized powders, a correct reaction path for the reduction process has been elucidated. The average particle size of nano powder synthesized was estimated from SEM as well as XRD as 78±12 nm and 61.3±2.0 nm respectively, and the values were found to be in good agreement. The particle size determined by XRD was upon applying the Rietveld refinement method and using isotropic Lorentzian Scherrer particle broadening parameter (LX) of refined peak profiles. From the average size of the particulates and from the specific surface area of LaB_6 (1.3 m^2/g) as determined by BET method, the number of unit crystals that might have constituted a nano-particulate of size 61.3±2.0 nm was estimated as 10^5 numbers from the crystallographic information of LaB_6.

Keywords: Magnesiothermic method; LaB_6; nanocrystals; leaching.

1. Introduction

Metal borides in general are of great importance as ceramic materials due to their high hardness, high heat and electrical conductivity, good abrasion, thermal shock and corrosion resistance properties, and for an excellent chemical stability at high temperatures [1-7]. Amongst all metal borides, rare-earth hexaborides (RB_6; where R=La,Ce,Pr,Nd,etc.) as refractory ceramics occupy a special place because of their low work function, which attributes to their high electron emissivity, super-conductivity, ferro-magnetism, narrowband semi-conductivity, etc. Lanthanum hexaboride (LaB_6) in these respects is especially important for its highest electron emissivity hitherto known, and also for its excellent vacuum stability. One of the few major areas of usage of LaB_6 is for its hot cathodic application either in a single crystal form or as coatings deposited by physical vapor deposition. Because of its low work function (2.6eV) and low vapor pressure at high temperatures, LaB_6 has been considered as the material of choice for thin film coatings applications for both decorative and hard coatings [8]. Ceramics composites containing LaB_6 are gaining more and more importance in application sciences particularly as support for transition metal catalysts [9]. Recent findings on nano-LaB_6 showed its high effectiveness to absorb near-infrared emissions, which opened the new field of potential applications in reducing solar heat gains [10]. The nano LaB_6 powder is particularly considered as a material of great interest for coating filaments, carbon nano tubes and silicon field-emitters to lower work function in order to improve their electron-emissivity [11]

Various synthetic methods are commonly used for the synthesis of nano metal borides, such as borothermal [12], carbothermal [13], magnesiothermic reduction and electrochemical synthesis in molten salt [14-15], solvothermal [16], combustion syhtnhesis (SHS) [17], mechanochemical [18] and floating zone method [19]. The synthesis of LaB_6 via magnesiothermal method is particularly beneficial due to the fact that they can be formed at relatively low reaction temperatures. In this work, pure LaB_6 nanocrystals were synthesized by magnesiothermic reaction using La_2O_3, B_2O_3, I_2 and Mg powders at 90 □C. The effect of stoichiometry and temperature on the synthesized nano-phase of LaB_6 were investigated in detail. Their microstructures and phase characteristics were studied by X-ray diffraction and electron microscopy. From the average size of the particulates (28.3 ± 3.0 nm) as determined

by Scherer formula and from the surface area (1.3 m^2/g) analysis, it was approximated that each particulate of the LaB_6 nano-powder was comprised of approximately 600 unit-crystals of LaB_6 in an average.

2. Experimental Method

2.1. Materials

As starting materials La_2O_3 (< 100 nm, 99.99%, Sigma Aldrich), B_2O_3 (545.74 μm, >98.00%, Eti Maden), I_2 (99.7%, 1-3 mm, Sigma Aldrich) and Mg (138.66 μm, ≥99.00%, Sigma Aldrich) were used for the synthesis of LaB_6. B_2O_3 was vacuum desiccated for more than 24 h prior to using in order to avoid any moisture ingress. All ball milling and magnesiothermic reduction processes were conducted under Argon gas (99.999%) atmosphere. 5 M Hydrochloric (HCl) acid solution was used for the purpose of leaching out MgO formed as a byproduct in order to produce pure form of nano-crystalline LaB_6 from the reaction mix.

2.2. Magnesiothermic Reduction

The pre-weighed stoichiometric powder mixtures of La_2O_3, Mg, B_2O_3 and I_2 were placed in a grinding vial in a glovebox, and then the powder mixtures were milled under Argon atmosphere for 3 hours at 300 rpm in a ball mill (Fritch, P6) to prepare refined homogenous blends with reduced particle size. All samples must be handled very carefully under Argon atmosphere and devoid of any oxygen, in order to evade the possibility of any explosive reaction. The magnesiothermic reduction of the ball-milled powder mixture was conducted in a quartz tube. The quartz tube containing the reaction powder mixture was gradually heated to 90 °C in an ash furnace maintaining a heating rate of 2 °C/min under Ar atmosphere. The magnesiothermic reduction process followed almost instantaneously as soon as the temperature reached 90 °C to form nano-particles of LaB_6 and MgO, $Mg_3(BO_3)_2$ and LaOI as byproducts. The product mixture obtained after the magnesiothermic reduction reaction was leached with 5M hydrochloric acid (HCl) acid solution at 70 °C for 45 min with magnetic stirring at 400 rpm to remove all unwanted phases from the mixture. After the acid leaching process was complete, the slurry was centrifuged to separate LaB_6 and then it was vacuum dried under 20 mbar pressure in a vacuum oven (Memmert VO-400) at 80 °C for 12h forming pure nanocrystalline powders of LaB_6.

For the preparation of LaB_6 nanocrystalline powders, four different starting powder mixture recipes were pursued to optimize the yield of LaB_6. The molar ratios of the mixtures of La_2O_3, Mg, I_2, B_2O_3 as shown in Table 1.

Table 1. Experimental conditions and the ratio of the powder mixtures used (La_2O_3:Mg:I_2:B_2O_3)

	A	B	C	D
Stoichiometry (mol)	1:44:6:12	1:48:6.6:13.3	1:58.5:8:16	1:88:12:24
Temperature (^oC)	90			
Period (min)	0-50			
Atmosphere	Argon			

2.3. Characterization of the powders

Malvern Mastersizer-2000 was used for the particle size analysis of all precursor powders used for the synthesis of LaB_6. The phase structure of the powders was determined by X-ray diffractometer (Rigaku D / MAX-2200) with Cu Kα radiation. A scanning rate of 4^o per minute was used to scan over the range between 2^o and 90^o (2θ). Identification of crystalline phases were determined by the files of International Center for Diffraction Data (ICDD) powder diffraction. Morphology of the powders were determined by scanning electron microscopy (SEM) (FEI Quanta-200F) and the surface areas of the powders were determined by BET method (Quantaochrome Nova 220E). From the SEM of the nano-powders, particle sizes were determined by using the image processing program ImageJ Analyzer software [20]. The crystal structure as obtained by the XRD's of the purified powders was refined with Rietveld method using General Structure Analysis System (GSAS) [21]. The initial atomic coordinates of La and B in the LaB_6 phase are given in Table 2 and full occupancy was assumed for La and B.

3. Results and Discussion

The average particle sizes (d_{50}) for the starting powders of La_2O_3 (*hexagonal*, ICDD Card No: 01-073-2141), Mg (*hexagonal*, ICDD Card No: 01-089-5003) and B_2O_3 (*cubic*, ICDD Card

No: 06-0297) used were about 5.4 µm, 137.6 µm and 597.9 µm, respectively. As starting materials not all of them had any similarity with respect to their sizes and size distributions. Iodine (*orthorhombic*, ICDD Card No: 00-043-0304) used for the synthesis was rather very large in size compared to other components of the powder mix. Nevertheless, the individual sizes of the ingredients were of limited significance as starting materials as they were all ball milled for their size refinement. The starting powder mixtures were refined in a high energy ball-mill for 3 hours for homogenization and reduction of their primary particle sizes. The employed ball-milling was quite aggressive maintaining a powder to ball charge weight ratio at 1:18 for comminution prior to carry out the magnesiothermic reaction.

For the purpose of optimizing the conditions of synthesis, four formulation samples of varying mixing ratios marked as A, B, C and D (Table1) were first homogenized and then subjected to heat treatment process to produce LaB_6 [22]. All handling and milling processes were performed under Ar atmosphere. The homogenized powder mixture of the reactants first sealed into an argon-filled container, and then gradually heated to 90 °C at an incremental rate of 2°C/min. At this temperature, the powder mixture reacted almost instantaneously forming LaB_6 and other reaction byproducts. However, it is to recognize, at temperatures below the melting point of iodine, iodine sublimates until the equilibrium vapor pressure is reached, where several independent equilibria are effectively possible during the reduction process. As reported by others for similar type of magesiothermic reductions [23, 24], in this co-reduction method of La_2O_3 and anhydrous boric acid by Mg in the presence of I_2, I_2 actually enables the reaction to happen at lower temperatures that other magnesiothermic reduction process with iodine. Iodine in all probabilities acts as a catalyst that can greatly reduce the activation energy of reactions between La^{+++} and B. Following the dissociation equilibrium of iodine, $I_2(g) \leftrightarrow 2I(g)$, both La and Mg can form metal iodides or other intermediates so the reaction can undergo at lower temperatures. Similar reactions without using iodine are not known to form hexaborides even at 650 °C [24].

Going by the conventional wisdom and as reported by other authors as well, the intuitive reaction path for the synthesis of LaB_6 using magnesiothermic reduction process [24-26], should have been as expressed in Eq. 1.

$$La_2O_3 + 27\ Mg + 6\ I_2 + 6\ B_2O_3 = 2\ LaB_6 + 21\ MgO + 6\ MgI_2 \quad (1)$$

However, the XRD pattern of the synthesized powders prior to leaching brought about the fact that the reaction was of very different nature in the presence of I_2 than it was originally thought to be. The XRD's of the as-prepared powders as shown in Fig. 1 revealed that the reaction products were actually the mixtures of LaB_6 (ICDD Card No:01-073-1669), $Mg_3(BO_3)_2$ (ICDD Card No:01-073-1541), MgO (ICDD Card No:01-075-1525) and LaOI (ICDD Card No: 01-073-2065) phases. The presence of MgO (*cubic, space group=Fm-3m, a=b=c=4.198 Å*), LaOI (*tetragonal, space group P4/nmm, a=b=4.144 Å, c=9.126 Å*), $Mg_3(BO_3)_2$ (*orthorhombic, space group=Pnnm, a= 4.497 Å, b=5.398 Å, c=8.416 Å*) and LaB_6 (*cubic, space group=Pm-3m, a=b=c= 4.157 Å*) phases were observed with all four reactions mixtures. Therefore, the magnesiothermic reduction reaction of La_2O_3 in the presence of I_2 does not follow as per the conventional understanding [21, 26, 27]. as stated in Equation 1, it rather follows as per the reaction given below in Eq 2. This mechanism is probably established for the first time for the synthesis LaB_6 nanocrystals produced by magnesiothermic reduction process using I_2.

$$2\ La_2O_3 + 34\ Mg + I_2 + 12\ B_2O_3 = 2\ LaB_6 + 2\ LaOI + 2\ Mg_3(BO_3)_2 + 28\ MgO \qquad (2)$$

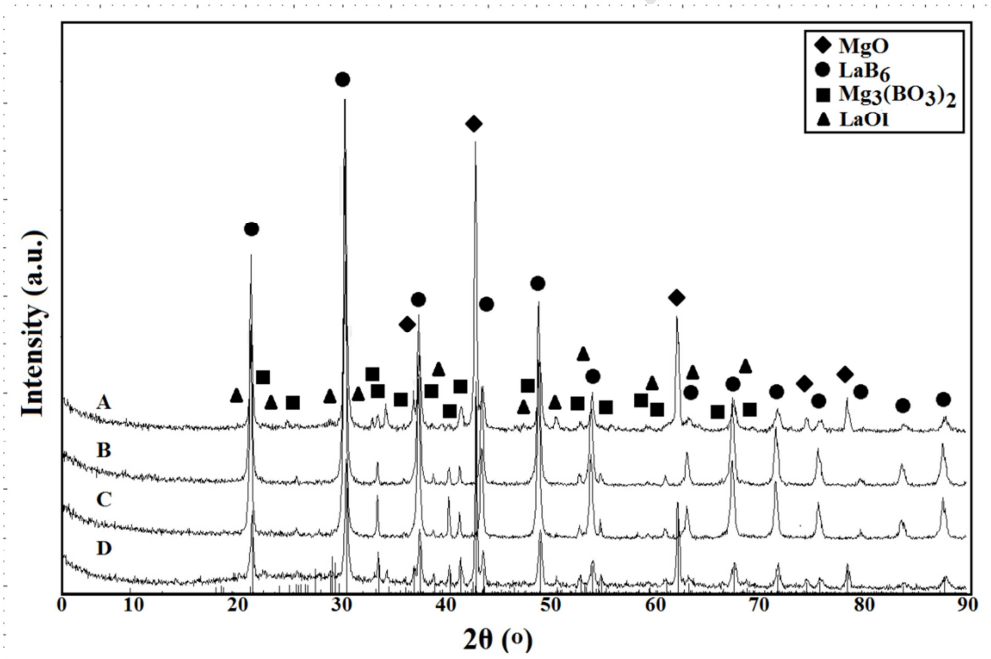

Fig. 1. XRD graphs of as-prepared powders obtained from the magnesiothermic reduction reactions using different molar ratios of the reactants, La_2O_3, Mg, I_2, and B_2O_3, (A: 1:44:6:12, B: 1:48:6.6:13.3, C: 1:58.5:8:16, D: 1:88:12:24, for starting powders of) XRD graph of powders obtained after explosive reactions with different molar ratios.

The standard Gibbs free energy (ΔG) and the standard enthalpy changes (ΔH) were determined using HSC Chemistry 6.0 software [28]. ΔG and ΔH changes for the reaction of the powder mixture La_2O_3+B_2O_3+Mg+I_2 to 2000 °C were calculated and plotted in Figure 2a. Figure 2a shows that the reaction of the starting powders at all temperatures between 0 to 2000 °C has a large negative Gibbs free energy and large enthalpy change. According to the estimation of the Gibbs free energy, the overall reaction of Eq. (2) is thermodynamically spontaneous (ΔG= −5450 kJ mol−1) and highly exothermic (ΔH=−6350 kJ mol−1) as reported elsewhere as well [26, 29]. Due to its high exothermicity, a massive internal heat is generated within the reacting species, and as an effect the internal temperature becomes much higher, which results in reduction of B_2O_3 by Mg to B. All subsequent reaction steps for such reduction process for the formation of LaB_6 are given below. It explains the role of I_2 in this low temperature magnesiothermic reduction process for the synthesis of LaB_6, where I_2 forms intermediate compounds with La that ultimately lead to form LaB_6 releasing iodine back .

$$I_2(g) \leftrightarrow 2I(g) \qquad (a)$$

$$2B_2O_3 + Mg \rightarrow Mg(BO_3)_2 + 2B \qquad (b)$$

$$La_2O_3 + 4I \rightarrow LaI_3 + 2LaOI \qquad (c)$$

$$2LaI_3 + 12B \rightarrow 2LaB_6 + 3I_2 \qquad (d)$$

The probable reaction steps as shown above indicated that the higher concentration of Mg can induce the formation of more LaI_3 by converting LaOI to LaI_3 according to the eqn. (e), and consequently the formation of more LaB_6.

$$LaOI + Mg + 2I \rightarrow LaI_3 + MgO \qquad (e)$$

The XRD's also confirmed that mechanistically higher concentration of Mg can force the reaction to form more LaB_6 and reduce the formation of LaOI, which also validates the proposed reaction pathway. As per the above reaction steps, a higher molar concentration of Mg must kinetically also favor the formation of MgO as shown in Eq.(e).

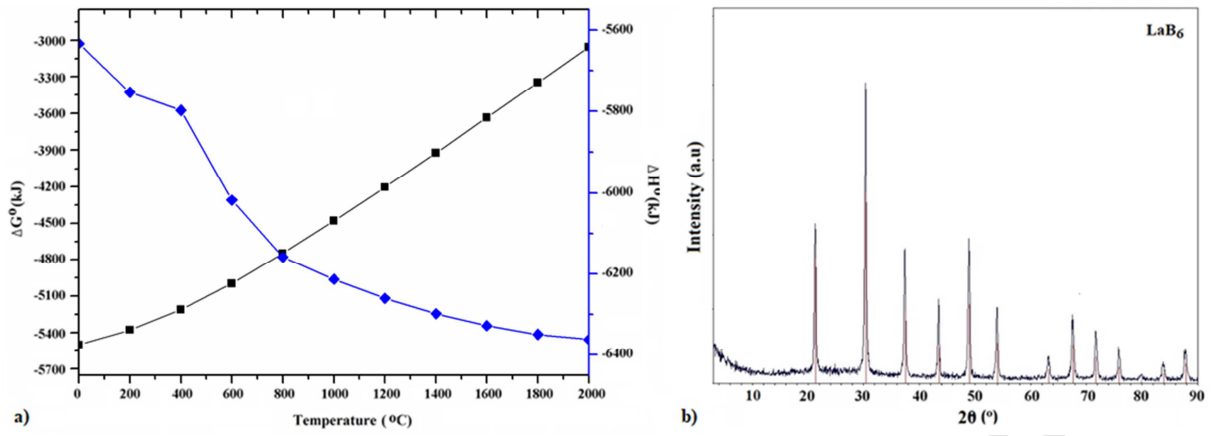

Figure 2. a) Gibbs free energy change (■) and enthalpy change (◆) versus temperature curves of the overall reaction in Eq.(2). b) XRD pattern of the LaB_6 nanocrystals

After a thorough and careful washing with 5 M HCl solution, the $Mg_3(BO_3)_2$, LaOI and MgO phases were removed from the synthesized powders. After leaching the powder was further washed with deionized water. The thoroughly leached and washed power was subjected to vacuum drying. The XRD pattern of the purified powder given in Figure 2b clearly showed that the final product of LaB_6 was completely free from any undesirable contamination and the average crystallite size of LaB_6 phase was determined as 28 ± 3.0 nm by well-known Scherrer formula.

Figure 3 presents the Rietveld refinement applied to the XRD pattern of the purified sample. The grey (plus) and black lines shows the purified powders and calculated pattern of the modelled structure, respectively. The difference of the observed and calculated patterns is plotted in the lower part of the figure as a solid trace. The vertical bars refer to the calculated allowed Bragg reflections. Single phase Rietveld refinement confirms the structure of LaB_6 in *Pm-3m* space group with the lattice parameters of $a=b=c=$ 4.153(2) Å. Table 2 presents the details of the basic crystallographic data for LaB_6. The diffraction peaks are well indexed and assigned to the parallel crystal plane of (100), (110), (111), (200), (210), (211), (220), (221), (310), (311), (222), (320) and (321). The obtained results are in good agreement with the previous data published in the literature [9, 24]. The diffraction data was *refined* on the *assumption* that the metal atoms would *occupy* the site 1a whereas non-metal *atoms would* be at the 6f site. The sharp and well-defined peaks in Fig. 3 indicated the high purity of the crystalline products. The average particle size was also determined as 61.3 ± 2.0 nm by using the isotropic Lorentzian Scherrer particle broadening parameter (LX) of refined peak profiles.

Because of the polycrystalline nature of the synthesized LaB_6 powder particles, the particulates are composed of many crystallites of varying sizes and orientations. Measuring crystallite sizes from XRD patterns is a well-known technic. SEM images revealed that individual crystallites within the relatively larger particle sizes.

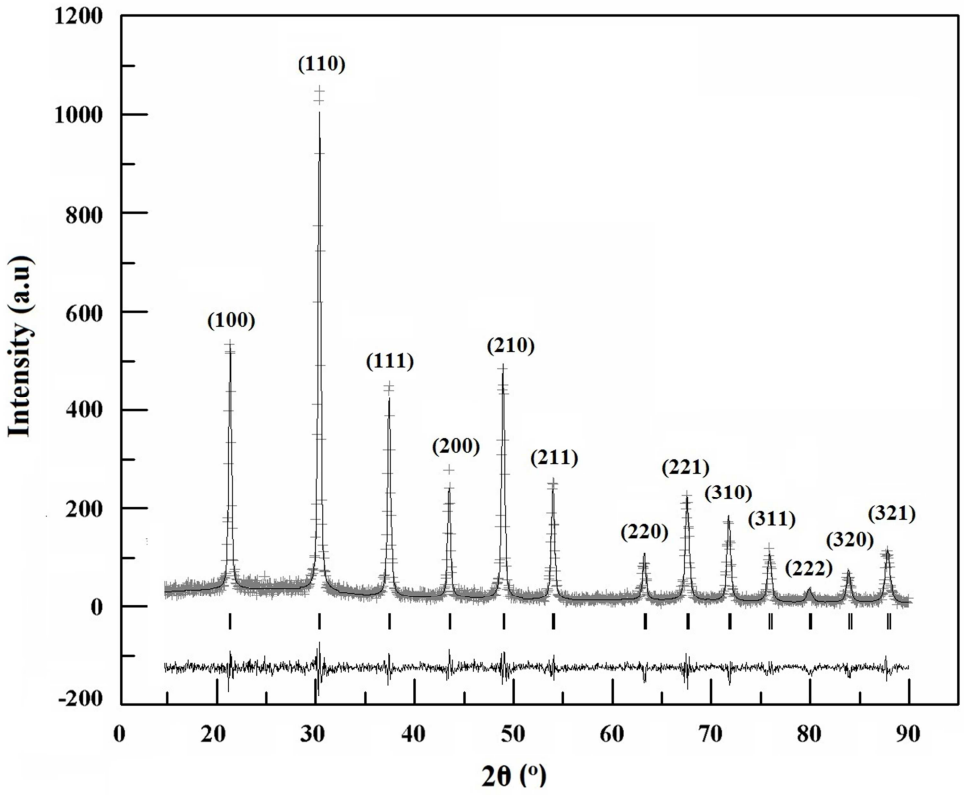

Figure 3. Rietveld refinement of LaB_6.

Table 2. Atomic positions and crystallographic data of LaB_6

Formula	LaB_6		Space group		*Pm-3m*
Crystal system	*Cubic*		Data points		1739
Unit cell dimensions (Å)	$a = b = c = 4.154(3)$ $\alpha = \beta = \gamma = 90°$		Unit cell volume ($Å^3$)		71.7(4)
2θ range refined	15-90°		R_p		0.1329
S (χ^2)	1.421		R_{wp}		0.1807
Atomic positions					
Atom	site	x	y	z	Uiso
La	1*a*	0	0	0	*0.0016(2)*
B	6*f*	0.2018(4)	0.5	0.5	*0.0027(3)*

SEM images of the purified powders are shown in Fig.4. LaB_6 nano-particles thus produced were in clustered forms of many particles. An approximate size of those sample was estimated as 78 ± 12 nm by ImageJ software. As expected, their agglomerations could have been due to the vacuum drying conditions during the purification steps. The similar observations were also reported elsewhere [26, 30]

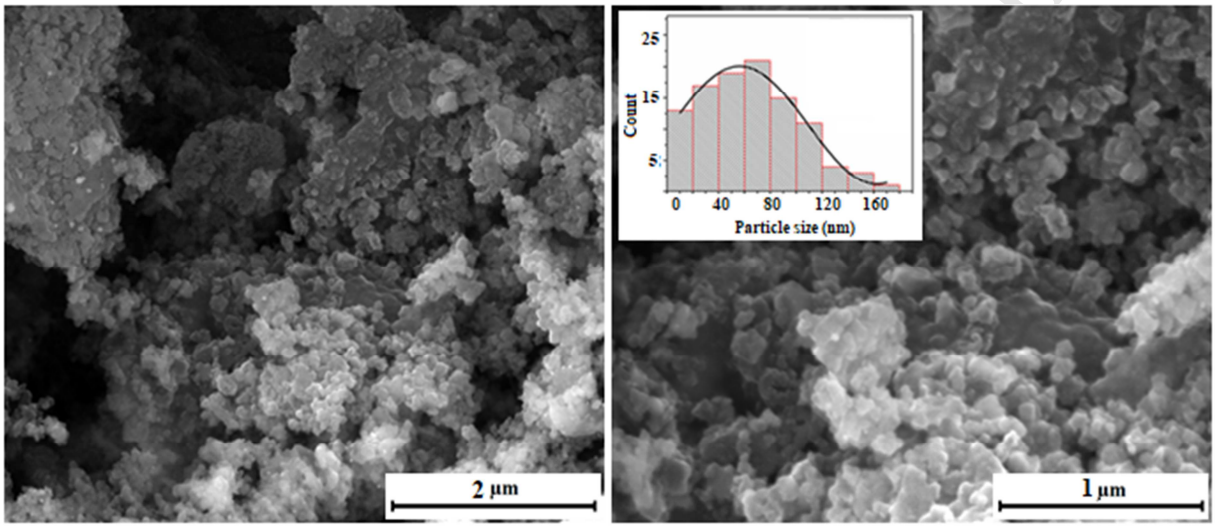

Fig 4. SEM images of purified LaB_6 nanocrystals

The average particulate size of LaB_6 phase was determined as 61.3 ± 2.0 nm and the specific surface area of the purified LaB_6 powder, 1.3 m^2/g, determined by BET method further signified that the nano-particulates are composed of many small LaB_6 units. The rationale of such approximation was realized from the structural information available on LaB_6 crystals. The crystal structure of LaB_6 is simple cubic (space group; Pm-3m), with Boron-octahedra in body-centered positions and La atoms at the corners of the unit cell. The crystal structure of LaB6 comprising two unit-cells is shown in Fig. 5 as an illustration. As it can be seen boron atoms in each unit are in the form of octahedral cage. The bond length of B6-B7 in adjoining cells is the shortest in the LaB_6 crystal structure. The crystal structure studies by Hossain et al delineated that in LaB_6 there was a coexistence of covalent, ionic, and metallic bonds, which probably explains the reason for the high thermionic emissions of LaB_6 [25]. Going by its stoichiometry, a unit crystal of lanthanum hexaboride comprises 12 units of LaB_6 ($La_{12}B_{72}$; Mol. Wt. 2447.4) constituting $2.5x10^{20}$ such unit crystals per gram. From the measured surface area ($1.3m^2/g$) and the average volume of each nano-particulate (considering spherical

sweeping volume for the nano-particles of LaB_6 of size 61.3 ± 2.0 nm for the sake of simplicity), the average mass of an individual particulate can be estimated in of the order of $5x10^{-15}$g (considering the density of LaB_6 as $4.72x10^6$ g/m^3). From that estimated value it can be visualized that each particulate of an average size of 61.3±2.0 nm might comprise around 10^5 numbers of unit-crystals to constitute a nano-particulate. A similar value was also obtained from the surface area approximation of the nanoparticles and from the BET surface area value.

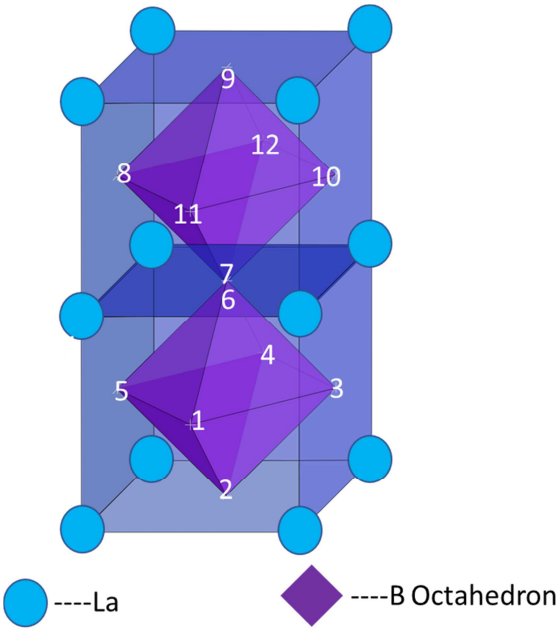

Fig. 5. In the crystal structure of Lanthanum hexaboride, two adjoining unit cells show the bonding between two adjacent octahedra of boron. The bond length of B6-B7 is the shortest distance in the structure.

4. Conclusion

A viable method of synthesizing a very pure form of LaB_6 nano-powders has been devised by adopting a low temperature synthetic route using La_2O_3, B_2O_3, Mg and I_2 under an inert atmosphere. The ball milling process increased the reactivity of the starting materials enabling the reaction to occur at temperatures around 90 ^oC. Removal of all byproducts by leaching and washing helped forming nano-LaB_6 powders in very pure forms. The reaction mechanism for the formation of LaB_6 was confirmed by XRD. From the specific surface area of the nano-powder (1.3m^2/g) and from the average size of the nano-particulates (61.3 ± 2.0 nm), it

appears from the crystallographic approximations that each small nano-particulate is probably constituted roughly by 10^5 numbers of unit-crystals of LaB_6 suggesting the fineness of the LaB_6 nano-powder synthesized by the present technic.

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Highlights

- Low temperature synthesis of pure LaB_6 via magnesiothermic method.
- Rietveld refinements of LaB_6 and its structural properties.
- Each particle seemed to be constituted by 10^5 numbers of unit crystal cells.
- Purification of unwanted phases by aqueous acid solution.