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The preparation and composition design of boron-rich lanthanum hexaboride target for sputtering



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ABSTRACT

Lanthanum Hexaboride (LaB₆) nano-film has been proved to be promising transparent thermal insulation material, while its properties are limited on purity and composition. High-purity LaB₆ polycrystalline powder was prepared through boron carbide reduction method in this work. A series of techniques such as scanning electron microscopy, X-ray diffraction, laser particle analyzer and inductively coupled plasma emission spectrometer were employed to characterize LaB₆ powder. As raising the content of La₂O₃ in reactants, more uniform, finer (2.686 μ m) and purer (99.5139 wt%) LaB₆ powder is prepared, with only 0.4434 wt% residual B₄C. The density of targets increases with the rise of sintering temperature and the extension of sintering time, while crystallite size increases simultaneously with the extension of sintering time, while crystallite size increases simultaneously with the extension of sintering time and microstructure of LaB₆ nano-film which is tentatively considered to be composed of LaB₆ nanocrystalline and amorphous microstructure of La and B atoms. The film LaB_{6.0627±0.02} was obtained when the ratio of B content in targets.

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1. Introduction

Lanthanum Hexaboride (LaB_6) has been widely used in applications such as cathode emission materials [1–3], decorative coatings [4,5] and sensors of high-resolution detector [6]. In recent years, LaB₆ cathode emission materials have been applied in plasma cathode. As a pioneering work, Schelm and Smith [7,8] added LaB₆ into polyvinyl butyral (PVB) and made them into polymer film. The results showed that LaB₆ is effective in near-infrared absorption (750–1200 nm) and visible transmittance (380–750 nm), raising a research upsurge on the optical properties of LaB₆ nano-film for the application on building glass and automotive glass.

Magnetron sputtering [9] is one of the best methods to prepare LaB_6 nano-film with uniform thickness, stable component and high purity. The preparation process of magnetron sputtering to prepare LaB_6 nano-film was studied by Xu, Zhao and Wang [10–13]. The component of LaB_6 film tends to deviate from the stoichiometric ratio because of different deposition rates between La atom and B atom, and there is no special LaB_6 target yet. Hence, a suitable

target as cathode is significant for obtaining high-performance LaB₆ nano-film.

In this report, Boron carbide reduction method was applied to prepare LaB_6 powder under vacuum condition. The effects of holding time, La_2O_3 content and purification treatment on the properties of LaB_6 powder were studied. And then vacuum pressureless sintering was employed to prepare boron-rich LaB_6 sputtering target. The influences of sintering temperature and sintering time on the density and structure of target were investigated. The correlation of component between LaB_6 films and its sputtering source boron-rich targets was established.

2. Experimental methods

LaB₆ micron powder was prepared by solid phase reaction using La₂O₃ powder (99.99% purity, particle size <1 μ m) and B₄C powder (99.9% purity, particle size 5–10 μ m) as raw materials. The LaB₆ powder synthesized above and B powder (99.9% purity, particle size <1 μ m) were used to prepare boron-rich LaB₆ target for sputtering.



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It is very difficult to remove residual B_4C from the synthetic products due to ultrahigh melting point and insolubility in acid and alkali, by contrast it is much easier for La_2O_3 . Therefore the content of La_2O_3 in reactants was increased to promote the reaction of B_4C and its influences on the morphology and crystallinity of La_6 powder were investigated. The molar ratio of La_2O_3 and B_4C were 1:3 and 1:2, respectively (will be called group 1:3 and group 1:2 in the following). The

mixed powder after ball-milling process was pressed into cylindrical samples [14,15], which were used to synthesize LaB_6 powder at 1600 °C for 2 h according to the following total reaction equation:

$$La_2O_3 + 3B_4C = 2LaB_6 + 3CO \uparrow \tag{1}$$

The surface of as-prepared samples was ground off to a depth of 1 mm to remove the impurity layer. Then the samples were pickled by 5% hydrochloric acid solution under vacuum condition at 70 °C for 3 h. In order to study the growth process of LaB₆ particles, a resintering process for the samples of group 1:2 at 1650 °C for 2–4 h was designed.

The mixed powder of LaB₆ and B with the ratio from 1:0 to 1:7.5 (B/La: 6–13.5) were used to prepared boron-rich LaB₆ targets. The green bodies were sintered at different temperature 1500–1650 °C for different time 3–7.5 h. LaB_x nano-films were deposited on SiO₂ substrates by DC magnetron sputtering at room temperature, using the as-prepared boron-rich LaB₆ targets as sputtering source. The chamber was evacuated to a pressure below 4.5×10^{-4} Pa before deposition, and then the sputtering pressure was controlled at 1.5 Pa by introducing Argon (99.9999% purity) at the flow rate of 40 sccm. The distance between target and substrate was kept at 55 mm when sputtering process was carried out at the power of 50 W (1.77 W cm⁻²) for 30 min, with bias Us -100 V and ion current density 5 mA/cm² without any intentional heating during and after the whole process. The typical thickness and deposition rate of LaB_x film were in the range of tens to thousands nanometers and a few to tens nm/min respectively.

The structure of prepared LaB₆ powder was analyzed by X-ray diffraction (XRD, DAMX-2500TC) in the range of 2θ 10–80° with scan rate of 0.1°/s using the K α radiation of Cu (λ = 0.154056 nm). Field emission scanning electron microscopy (FESEM, JSM-6700F) with EDS (SUPRA™ 55) was used to observe the surface morphology and measure the components of LaB₆ powder and its boron-rich targets at an accelerating voltage of 3 kV and current of 23 µA. The size and distribution of LaB₆ powder was measured by laser particle analyzer (Beckman Coulter LS13320). Rockwell hardness tester (HD-1875) was employed to test hardness of boron-rich LaB₆ targets, with load at 30 kg. The samples with size $3 \text{ mm} \times 4 \text{ mm} \times 35 \text{ mm}$ were prepared for flexural strength test by three point bending beam method at room temperature, with span 25 mm and loading rate 0.5 mm/min. Step profiler (DEKTAK 150, Veeco) was used to measure the thickness of films and then the deposition rates were calculated. Composition analysis of the synthesized powder was conducted by inductively coupled plasma emission spectrometer (ICP, Optima 2100 DV) and carbon-sulfur Analyzer (CS-8800). The relative atomic ratio of La and B in LaB₆ nano-film was determined by X-ray photoelectron spectrometer (XPS, SCALAB250) using the K α radiation of Al and the scanning time was 90 s.

3. Results and discussion

3.1. The preparation of high-purity LaB₆ micron powder

The formation of LaB₆ powder is detected by XRD and FESEM (Figs. 1 and 2). The high and sharp characteristic diffraction peaks of LaB₆ indicate that LaB₆ polycrystalline powder has been prepared. The synthesized LaB₆ powder has slight (100) preferential growth. The calculated lattice parameter of purified LaB₆ powder of group 1:3 is 4.16688 Å, and it is 4.16676 Å for the sample of group 1:2. The calculated lattice parameters are both higher than the theoretical value (4.1566 Å), which is attributed to the existence of micro-strains. Most of the impurities had been removed after pickling and there is not any observable peaks of impurities for the samples of group 1:2, while there is one indelible impurity peak $(2\theta \ 33^\circ)$ for group 1:3 as shown in the partial amplifying views (Fig. 1b and c) of the box part in Fig. 1a. The SEM images show that after pickling LaB₆ particles have a smoother and cleaner surface and the particles that were bound together with impurities disperse from each other. The LaB₆ powder of group 1:2 contains fewer impurities after pickling (Fig. 2b') compared with the powder sample of group 1:3. Meanwhile, the morphology of the powder particles of group 1:2 after pickling is closer to cube and the size of particles is more uniform than the sample of group 1:3.

The existence of agglomerates (indicated by the arrows in Fig. 3a) would be harmful to the structural uniformity and density of target. A repressing and resintering process at 1650 °C for the samples of group 1:2 was performed to weaken the agglomeration. There is not an obvious effect of the resintering process on the phase structure. SEM images show that LaB₆ powder after resintering for 2 h has better dispersion due to the complete growth, while



Fig. 1. XRD patterns for LaB₆ powder before (1,3) and after hydrochloric acid pickling (2,4) synthesized using different raw materials ratio: (1,2) La₂O₃:B₄C = 1:3 (3,4) La₂O₃:B₄C = 1:2.

as the time extends the particles grow bigger and there are many small fragments on the surface of bigger particles (Fig. 3c). These small fragments which turned up during the grinding process due to the high brittleness of LaB_6 were removed mostly by settling separation (Fig. 3c').

The reduction of crystallite size would bring positive effects on the strength of target and the deposition rate of LaB_6 nano-film due to the increase of the proportion of highly reactive grain boundary. The effects of resintering time of LaB_6 powder and sintering time of targets on the crystallite sizes were investigated. The crystallite size D was calculated from the full width at half maximum (FWHM) of LaB_6 (110) peak obtained by XRD according to the following formula [16]:

$$D = (K\lambda)/(\beta\cos\theta) \tag{2}$$

where β is FWHM corrected by instrument width correction curve. *K* is Scherrer constant (0.943 for cubic particles) and λ is the wavelength of incident X-ray (1.54056 Å). The results show that the raw materials ratio has only a small impact on the crystallite size of synthesized LaB₆ powder. The crystallite size of LaB₆ powder increases and becomes faster with the extension of resintering time (Fig. 4a). The crystallite size of LaB₆ targets increases with the extension of sintering time and grows rapidly when the time was beyond 4.5 h (Fig. 4b).

The size and its uniformity of LaB_6 particles have a significant impact on the density of target. And the gas in big sealed pores in the target would bring harmful effects to the growth of film during sputtering process. The size distribution of LaB_6 powder (Fig. 5) reveals that the mean particle size for the sample of group 1:2 is smaller than that of group 1:3. The larger size part and the tail in the small size side of the distribution curve are eliminated through pickling treatment due to the removing of impurity phases, which is well consistent with the previous analysis. The distribution



Fig. 2. SEM images of LaB₆ powder before and after pickling (hydrochloric acid) synthesized using different raw materials ratio.



Fig. 3. Effects of resintering time on the morphology of LaB_6 powder: (a) 0 h, (b) 2 h, (c) 4 h and (c') 4 h, settling separation.



Fig. 4. Effects of resintering time of LaB₆ powder (a) and sintering time of targets (b) on the crystallite sizes of LaB₆ determined from the FWHM of LaB₆ (110) peak.



Fig. 5. Size distribution of LaB₆ powder.

curve became closer to normal distribution and the standard deviation (σ) decreased with the extension of resintering time. The LaB₆ powder that was resintered for 2 h has the smallest mean size 2.686 µm. As resintering time further increases, the particles grow up obviously, which is well consistent with the SEM results (Fig. 3).

A more accurate determination of the content of each component in the powder was provided to characterize the purity of LaB₆ powder (Table 1). The results show that there are trace amounts of impurities such as carbon which is mainly from residual B₄C powder, and silicon which is mainly from the raw materials and environmental pollution, etc. The results of XRD (Fig. 1) and EDS, however, show that there is not C atom in LaB₆ powder. The contradiction is due to the lower sensitivity of XRD for C element and the interference of LaB₆ layer around residual B₄C [17]. From the calculated value, it could be reconfirmed that most of residual La₂O₃ was removed by pickling treatment. There are several reasons for the negative value turned up at the content of La₂O₃. Firstly, B₄C is very difficult to be combusted completely during CS analysis owing to the high melting points, resulting in the reduction of test value compared to actual one. And there are

certain errors for the calculation based on the premise that the residual C atoms of purified samples were all from B_4C and the excess La atoms were all from La_2O_3 . The calculated content of B_4C for the sample of group 1:3 after pickling is 1.2422 wt%, and it is 0.4434 wt% for the sample of group 1:2, which demonstrates the effect of excess La_2O_3 on promoting the complete reaction of B_4C . The LaB_6 powder that was synthesized using excess La_2O_3 in reactants achieves 99.5139 wt% purity after purification.

3.2. Design and preparation process of boron-rich LaB_6 sputtering target

The effects of sintering temperature and sintering time on the densities of targets were shown in Fig. 6. The density of targets increases with the increase of sintering temperature (Fig. 6a). The density of targets increases with the extension of sintering time and the upward trend slows down toward a stable value of about 2.48 g cm⁻³ (Fig. 6b). Reasons for the increase of density lie in the rise of kinetic energy and the removing of pores. During the process of sintering, the pores would transform from connected pores into sealed pores, then balling, narrowing and disappearance due to the movement of particle interface. The density is improved by the increase of kinetic energy of atoms when the temperature increased, which is in favor of the movement of particle interface and the removing of the pores. However, to further increase temperature at such a high temperature would largely increase the cost and the burden of apparatus. Therefore, comprehensive weighting the effects of sintering temperature and sintering time on density and crystallite size, the optimal sintering parameters are 1600 °C and 4.5 h.

The added B promotes the sintering of target and the target B/La = 12.5 has better mechanical property than the target B/La = 6. Fig. 7 shows that the hardness and flexural strength of boron-rich LaB_6 targets both increase with the rise of B content. The cause is that the introduction of B powder which has lower melt point compared with LaB_6 promotes the slip of interface and the diffusion of atoms, transforming connected pores into sealed pores and forming more chemical combination (Fig. 8b). It could be found from the SEM micrographs of cross-section of LaB_6 targets that, eliminating the effects of pits, the distributions of B and La elements for the target B/La = 6 are well consistent (Fig. 8a). The

Table 1

Composition analys	is of purified	LaB ₆ powder s	ynthesized using	g different raw	materials ratio.
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Raw materials (La ₂ O ₃ :B ₄ C)	La (wt%)	B (wt%)	C (wt%)	B ₄ C (wt%)	LaB ₆ (wt%)	La ₂ O ₃ (wt%)	Other impurities (wt%)
1:3	67.2726	32.4160	0.2698	1.2411	98.7896	-0.0723	0.0416
1:2	67.8490	32.0223	0.0964	0.4434	99.5139	0.0104	0.0323



Fig. 6. Variation of the density of boron-rich LaB₆ targets with sintering temperature (a) and sintering time at 1650 °C (b).



Fig. 7. Mechanical properties of LaB_6 and boron-rich LaB_6 targets: (a) hardness (b) flexural strength.

content of B is higher on the edge of particles than inside for the target B/La = 12.5 (Fig. 8b). This indicates that LaB_6 particles are surrounded by smaller B particles and big pores are filled up with B particles. This result could be further confirmed from the SEM image of cross-section without polishing (Fig. 8c), which

demonstrates that the content of B in the surface of particles is much higher.

The composition of LaB₆ nano-film was measured by XPS. Fig. 9a and b shows an example for the XPS fitting results of the LaB_6 nano-film that was deposited using the target B/La = 12.5. The B 1s and La 3d5/2, 3d3/2 core level spectra of LaB₆ nano-films reveal that the chemical states of B and La atoms are not single. The peaks of La 3d5/2 core level lies in binding energy 837.3 eV and 835.7 eV, from which two components LaB_6 [18,19] and La are identified. The peaks of B 1s core level at 187.23 eV and 187.4 eV are approximately corresponding to LaB₆ [18,19] and amorphous B [20]. The LaB₆ nano-film is tentatively considered to be composed of LaB₆ nanocrystalline and amorphous microstructure of La and B atoms [21]. There is not obvious diffractive peaks could be found in the XRD spectra (Fig. 9c), which is attribute to the stronger surface scattering effect caused by finer grains and the interference of the metastable structure of LaB₆ on XRD test. The crystallinity and grain size of LaB₆ nano-film decrease with the increase of B content in targets [22]. For a certain substance, the binding energy of electron in a certain atomic level is constant. Hence, the relative atomic ratio of B and La $(R_{B/I,a})$ were calculated by measuring the kinetic energy of photoelectrons according to the following formula [23,24]:

$$R_{B/La} = (I_B/S_B)/(I_{La}/S_{La})$$
(3)



Fig. 8. Micrographs and composition analysis of LaB₆ target cross-section. (a)(a')(a") are the micrograph, composition distribution of lanthanum and boron of LaB₆ target with B/La = 6 after polishing, respectively; (b)(b')(b") are the corresponding results of LaB₆ target with B/La = 12.6 after polishing; and (c)(c')(c") are the results of the same target as (b) before polishing.



Fig. 9. Chemical and structure characteristics of LaB₆ films: fitting X-ray photoemission spectra of (a) B 1s and (b) La3d core level, and (c) XRD patterns of LaB₆ nano-films for the sample deposited by the target B/La = 12.5. (d) The correlation of the composition between the LaB₆ nano-films and boron-rich targets.

Table 2 Thickness and deposition rate of films using $LaB_6 + xB$ targets.

x	Thickness h (nm)	Deposition rate a_D (nm/min)
0.0	625	20.83
3.0	500	16.67
4.0	409	13.63
6.0	429	14.30
6.5	318	10.60
7.5	273	9.10

where I_B and I_{La} are the peak areas of B and La elements respectively, and S_B and S_{La} are the sensitivity factors. The correlation of atomic ratio of B and La between films and targets was established (Fig. 9d). The corporation of B atom in LaB₆ nano-film increases with the increase of B content in targets. The film with composition $LaB_{6.0627\pm0.02}$ was obtained when the atomic ratio of B and La of sputtering target reached 12.5. The cause for the dramatically fall of B content in films than in targets is the significant dispersion effect of B during the sputtering and deposition process. The electric and magnetic fields have a smaller bound effect for B ion and the low relative atomic mass of B makes it easier to deviate from the deposition direction. Generally, the phenomenon that sputtered B reacts with the oxygen presented in a residual atmosphere of the deposition chamber and B is released from the film as B₂O₃ gas will also causes the decrease of B content in the film [25]. However, B has higher chemical inertness than La which means that La is easier to react with O. In order to get clear on this question, two more films were prepared under pressure $2.5\times 10^{-4}\,\text{Pa}$ and 6.5×10^{-4} Pa, respectively. While the results of ICP test show that the effect is negligible. Therefore, the reaction of sputtered B with O is not considered to be the cause of the enormous difference of B content between films and targets.

The measured thickness of films and the calculated deposition rates were shown in Table 2. The thickness and deposition rate decrease with the increase of B content in targets. This indicates that B has lower deposition rate compared with La, so that when the content of B increases the number of La that deposited in the substrate is dramatically decreased while the amount of B does not increase in a same extent. This result is well consistent with the above analysis.

4. Conclusion

The main conclusions of this work are shown in the following:

- (1) As raising the content of La_2O_3 in reactants, uniform, fine (2.686 µm) and highly pure (99.5139 wt%) LaB_6 polycrystalline powder was prepared by boron carbide reduction method at 1600 °C for 2 h, resintering process at 1650 °C for 2 h and pickling treatment.
- (2) The density of targets increases with the increase of sintering temperature. The density of targets increases with the extension of sintering time and the upward trend slows down toward a stable value of about 2.48 g cm⁻³, while the crystallite size increase with the extension of sintering time simultaneously. Big pores are filled up with B particles which promote the sintering of target as well. The hardness and flexural strength of boron-rich LaB₆ targets both increase with the rising of B content. In this study, the LaB₆ target that was sintered at 1600 °C for 4.5 h is the optimal one.
- (3) The LaB₆ nano-film is tentatively considered to be composed of LaB₆ nanocrystalline and amorphous microstructure of La and B atoms. The proportion of B atom in LaB₆ nano-films

increases with the increase of B content in targets and presents an enormous reduction than the B content in targets. The film with composition $LaB_{6.0627\pm0.02}$ was obtained when the atomic ratio of B and La of sputtering target reached 12.5. The thickness and deposition rate decrease with the increase of B content in targets, which indicates that B has lower deposition rate than La.

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