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Synthesis of LaB_6 from BN and lanthanum-citrate-hydrate

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Lanthanum hexaboride was synthesized by reacting a powdered mixture of hexagonal boron nitride and lanthanum-citrate-hydrate carbonized substance which had been prepared by heating lanthanum-citrate-hydrate at 1000° C in a nitrogen atmosphere. The optimum conditions for the synthesis were a ratio of boron to lanthanum in the starting mixture between 5.0 and 6.0 with heating in the temperature range 1480 and 1600° C in an evacuated atmosphere.

1. Introduction

Hexaborides of lanthanum have been synthesized by many methods: electrolysis of a melt comprised of lanthanum salts and borates [1–3]; the reaction of the oxide of lanthanum with boron [4–10], with boron carbide [9, 11–13], and with a mixture of boron and carbon [9, 10]; the reaction of a mixture of lanthanum oxide and boron trioxide with carbon [9, 14], and with magnesium [15]; and the direct reaction of each element [16]. Some of the products from these processes are in the form of blocks, large grains, or fine powder in the size range 2 to 8 μm.

The present paper deals with a new method to synthesize lanthanum hexaboride (LaB_6) from hexagonal boron nitride (BN) and lanthanum-citrate-hydrate carbonized substance (LCC) at a temperature higher than 1480° C *in vacuo*. The preparation of LCC from lanthanum-citrate-hydrate, the effects of B/La ratio in the BN–LCC mixture and of the heating temperature on the final products were investigated by X-ray diffraction and scanning electron microscopy.

2. Experimental procedure

2.1. Chemicals

The chemicals employed were 99.99% pure La_2O_3 (Shietsu Chemical Co, Ltd), reagent grades of citric acid and acetic acid (Wako Pure-chemical Co, Ltd), and 99.99% pure hexagonal BN powder, 1 to 5 μm in size (Denki-kagaku Co, Ltd).

Lanthanum-citrate-hydrate was prepared by adding an aqueous solution of citric acid to acetic acid in which La_2O_3 had been dissolved (molar ratio of citric acid to $La_2O_3 = 2:1$). The precipitate was washed with water, followed by drying. The LCC employed for syntheses of LaB_6 was prepared by heating the lanthanum-citrate-hydrate in N_2 at 1000° C. One weight part of the original lanthanum-citrate-hydrate turned to 0.478 parts of LCC at 1000° C and this LCC changed to 0.412 parts of La_2O_3 in oxygen. From this weight change ratio, the lanthanum content in the LCC was determined. The LCC thus prepared could be easily pulverized with an alumina mortar.

2.2. Carbonization of lanthanum-citrate-hydrate

The weight of the lanthanum-citrate-hydrate in the carbonizing process was measured using a balance, with a heating rate of 3.5° C min^{-1} up to 1000° C in N_2. Differential thermal analysis (DTA) of the sample was made with 5° C min^{-1} up to 500° C in Ar using alumina as the standard.

The lanthanum-citrate-hydrate was heated in a horizontal quartz tube wound with nichrome wire and with one end of the tube connected to a sampling tube. In order to analyse the gas evolved during the heating process, the temperature of the sample was raised quickly to a certain temperature. While the furnace was kept at that temperature for 40 min, the evolved gas was taken at intervals of

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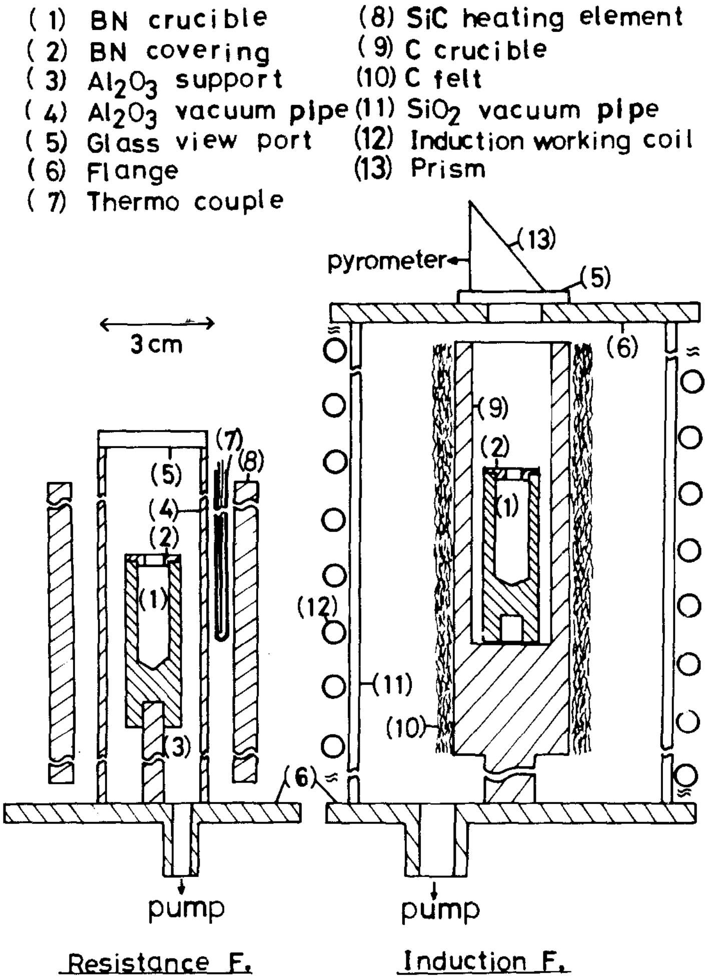

Figure 1 Arrangements of the furnaces.

several minutes and analysed. In sampling for chromatographic analysis, He or Ar was passed in the furnace, depending on the species of the gas to be analysed; for mass spectrometry, He was used. Then, the temperature was raised again quickly and the same procedure was repeated several times.

2.3. Synthesis of lanthanum hexaboride

Syntheses of LaB_6 were carried out in a BN crucible placed in a SiC resistance furnace or in an induction furnace, the arrangement of which is illustrated in Fig. 1. In the latter furnace, the BN crucible was positioned in an outer one of graphite which served as a susceptor. Both furnaces were evacuated with a diffusion pump. Gaseous pressure measured by an ionization gauge reached down to 2×10^{-6} Torr in the resistance furnace, while that in the induction furnace fell no lower than 1×10^{-4} Torr, since foreign gas had been given off from the graphite susceptor and the carbon felt. The temperature of the sample in the induction furnace was measured using an optical pyrometer.

An appropriate proportional powdered mixture of BN and LCC was heated at ~ 1550° C in the induction furnace and the heated mixture was pulverized. This procedure was repeated at least twice to complete the reaction.

3. Results

3.1. Carbonization of lanthanum-citrate-hydrate

Thermogravimetric and DTA curves of lanthanum-citrate-hydrate are shown in Fig. 2, in which only endothermic reactions are observed in the latter and the weight of the sample becomes constant at 950° C as seen in the former. In general, the gas evolution became vigorous with increasing temperature; however, the amount of the gas decreased with time under isothermal conditions and the gas composition varied simultaneously. The species of gas evolved at different temperatures

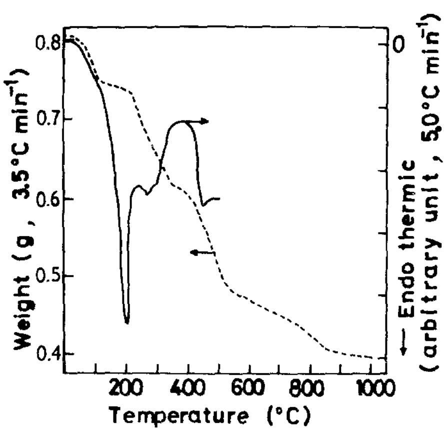

Figure 2 TG and DTA curves of lanthanum-citrate-hydrate.

are indicated in order of quantity in Table I. The amount of gas evolved at 1000° C was very small suggesting that the weight of the heated product, e.g. LCC, became constant at this temperature, which is similar to the thermogravimetric result.

3.2. Optimum mixing ratio of BN and LCC

The quantity of unreacted BN in the synthesized LaB_6, which was represented by the ratio of X-ray diffraction peak-height for $d = 3.33$ Å in BN and for $d = 2.94$ Å in LaB_6 is plotted against the boron: lanthanum ratio in the starting mixture (B/La) in Fig. 3. Extrapolation of the curve to zero can be considered to give the equivalent atomic ratio of boron and lanthanum for the formation of LaB_6. In the present investigation, this ratio appears to lie between 5.0 and 6.0.

3.3. Gas evolved during heating

The pressure of the gases evolved from LCC alone and from the BN–LCC mixture having the same B/La ratio of 5.0 were measured during heating to 1530 and 1570° C with heating rates of 320 and 180° C h^{-1}, respectively. As shown in Fig. 4, the evolution of gas from LCC alone became vigorous above 1200° C and reached a maximum at 1400° C. On the other hand, that from the mixture gradually increased with temperature and exhibited a sharp peak at 1550° C.

TABLE I Gas evolved from lanthanum-citrate-hydrate during the carbonizing process

Temperature (° C)	Species
100	H_2O
300	$H_2O > CO_2$
400	$H_2O > CO_2 > H_2$
500	$CH_4 > CO_2 > H_2 > H_2O > CO$
800	$CO > H_2 > CO_2 > H_2O$
1000	H_2

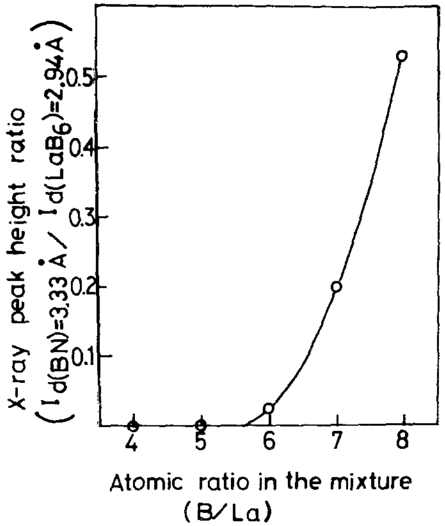

Figure 3 B/La ratio in BN–LCC mixture versus residual BN in the heated products.

Measurement of the pressure of gas evolved from the mixture having B/La ratio of 6.4 and 5.3, under step-wise isothermal condition, i.e. the same manner of heating process described above, was also made. The results presented in Fig. 5, together with the thermal history, indicate that the main reaction in the former mixture proceeds at 1450° C for 5.5 h. The reaction of the latter mixture proceeds at 1520° C for 2 h and the residual gas seems to evolve at a temperature higher than 1600° C.

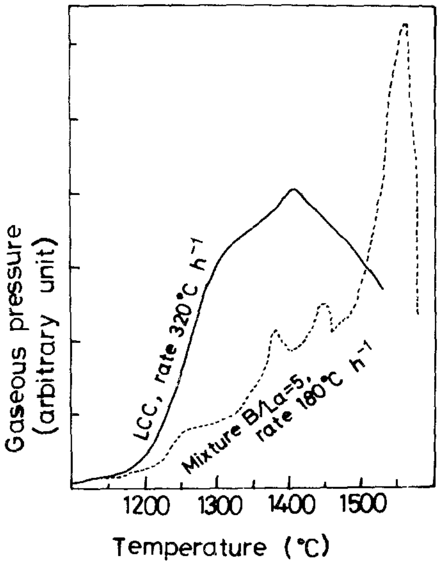

Figure 4 Change in pressure of the gas evolved from LCC alone and from the BN–LCC mixture (B/La = 5.0) with increasing temperature.

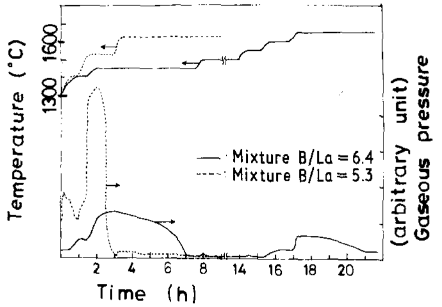

Figure 5 Change in pressure of the gas evolved from the BN–LCC mixture (B/La = 6.4 and 5.3) during stepwise heating with time elapse, along with thermal history.

3.4. Appearance of the synthesized products

The conditions for synthesis and observations made on the products are summarized in Table II. Scanning electron micrographs of the products are reproduced in Fig. 6.

4. Discussion

In test 1, LaB_6 was synthesized at a temperature of 1480° C, which is near to 1450° C at which gas evolution from the BN–LCC mixture became violent, as observed in Fig. 5. The synthesized LaB_6 contained BN together with unidentified material. This LaB_6 appears to be formed on the residual BN, as shown in Fig. 6a. The final product in test 2 also contained residual BN and unidentified material, and the former maintained its laminar shape at 1520° C (Fig. 6b). This indicates that either the previously formed BN diffuses out through the coating layer of LaB_6 or the unidentified material formed from the excess LCC diffuses into the LaB_6 layer at 1600° C, which nearly corresponds to the temperature at which the residual gas began to evolve (Fig. 5).

The LaB_6 obtained in test 3 and that in test 4, in which the B/La ratio of each starting mixture was 5.0, did not contain any free BN. The former, which was synthesized in the induction furnace, was massive as can be seen in Fig. 6c, whereas the latter synthesized in the resistance furnace had a distinctly rectangular parallelepiped shape (Fig. 6d). The same comment applies about the cause of the difference in the shape. For instance, except for tests 4 and 6, the synthesized LaB_6 contained an unidentified impurity. The X-ray diffraction peaks for the impurity disappeared when the product in test 5 had been leached with water, whilst the impurities in each product of tests 1, 2, and 3 were observed to remain even after water leaching. From these observations, it is envisaged that two kinds of impurity exist in the synthesized products: one may come from the carbon used as the susceptor and the other may be carbonaceous residue formed by thermal decomposition of LCC in the induction furnace. The latter impurity seems to affect the morphology of the synthesized LaB_6.

In Fig. 6e, the existence of small spherical shapes and rounded edges of LaB_6 can be observed. These are probably molten products of lanthanum metal, lanthanum carbide, etc., which might be formed by self-decomposition of the excess LCC.

TABLE II Conditions for LaB_6 syntheses and observation on the products

Test	Condition				Products			
	B/La in BN-LCC mixture	Furnace	Heating		Fig.	Dimension (μm)	Appearance	Impurity
			Temp. (° C)	Duration (h)				
1	6.0	I*	1480	3.9	6a	0.4–1.5	Thick plate	BN, unidentified‡
2	7.0	I	1520	4.0	6b	0.3	Irregular	BN, unidentified‡
3	5.0	I	1580	3.7	6c	1.7–3.5	Massive	Unidentified‡
4	5.0	R†	1600	3.0	6d	1.5–2.0	Rectangular parallelepiped	–
5	4.0	I	1650	1.3	6e	2.0–6.0	Rounded edges and sphericals	Unidentified‡ Unidentified§
6	8.0	I	1850	4.5	6f	2.0–6.0	Portion molten	–

*Induction furnace.
†Resistance furnace.
‡Unidentified material, possibly came from the graphite susceptor or thermally decomposed carbonaceous residue.
§Unidentified material, possibly formed by self-decomposition of the excess LCC.

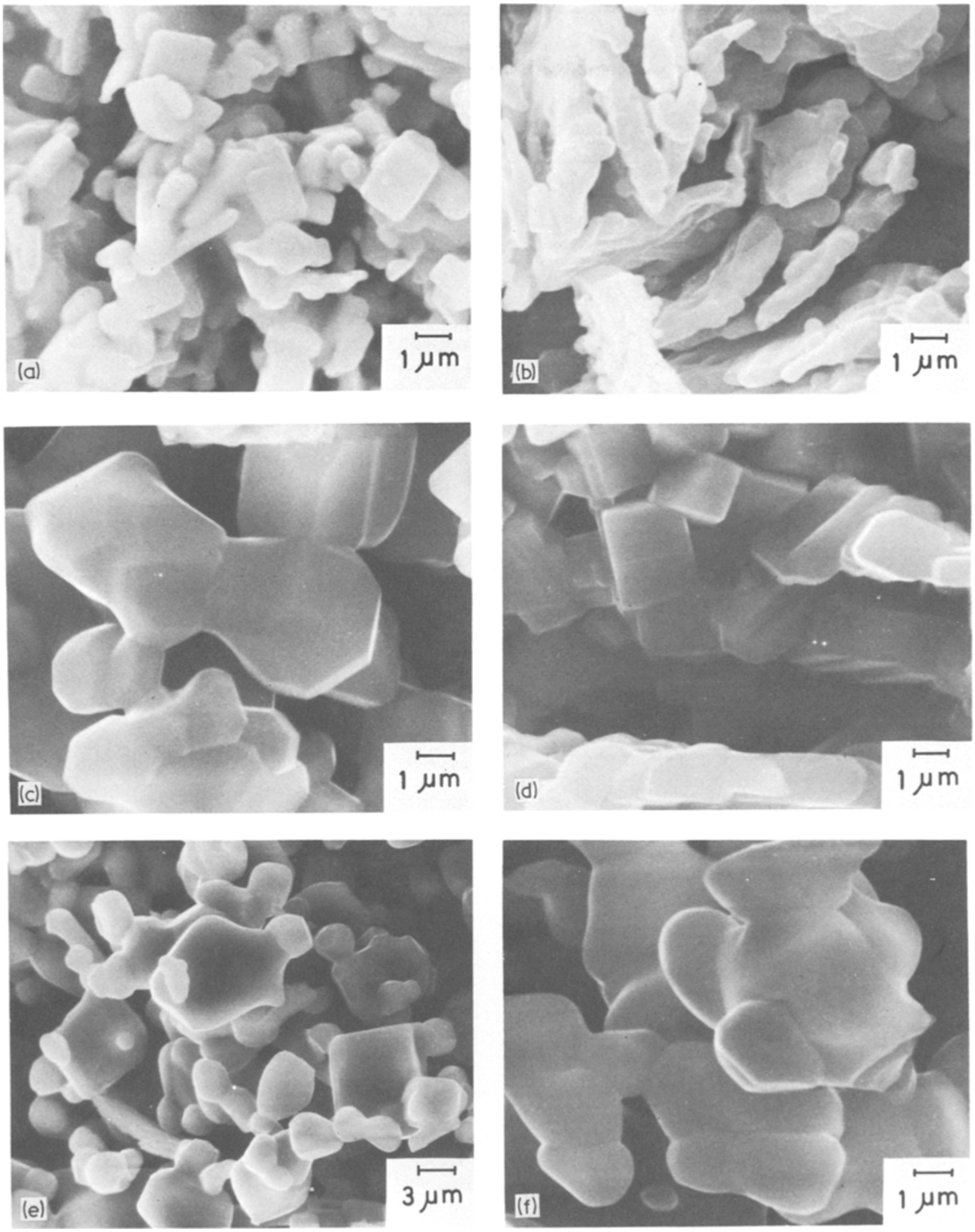

Figure 6 (a) to (f) Scanning electron micrographs of the synthesized LaB_6.

Formation of lanthanum metal or carbide is supported by the fact that the final heating product of LCC alone in the experiment to obtain the curve for LCC alone in Fig. 4 was electrically conductive grey material, which was converted to lanthanum hydroxide by exposure to air at room temperature for a few days.

In test 6 in which the B/La ratio of the starting mixture was 8.0, neither BN nor unidentified impurity was detected in the final product. On the contrary, considerable amounts of BN remained in the heated product of the mixture having the same B/La ratio at 1550° C, as shown in Fig. 3. This could be due to the known sublimation of BN or to decomposition into nitrogen and amorphous boron – the equilibrium nitrogen pressure at this stage is 1×10^{-5} Torr at 1550° C and 2×10^{-5} to 3×10^{-5} Torr at 1650° C [17–18].

A critical temperature which affects the grain growth of the LaB_6 synthesized from BN–LCC mixtures seems to exist between 1520 and 1580° C, growth being promoted beyond this critical temperature (Figs. 6a–f).

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