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Floating Zone Growth and High Temperature Hardness of Rare-Earth Hexaboride Crystals: LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6

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Single crystals of rare-earth hexaborides, LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6, were prepared by the floating zone method. Their crystal quality increased as the atomic number of the rare-earth metals increased. The difference in the quality was explained from the high-temperature hardness and the growth temperature. © 2000 Academic Press

Key Words: **floating zone growth; crystal; hardness; LaB_6; CeB_6; PrB_6; NdB_6; SmB_6.**

1. INTRODUCTION

The floating zone method is well suited to preparing large refractory crystals, but subgrain boundaries are formed by thermal stress due to a steep temperature gradient (1). Recently, high-quality refractory crystals, free of the boundaries, were prepared by controlling composition of a molten zone (the traveling solvent floating zone method) (2–4). The improvement in quality was explained by increase in the mechanical strength due to decrease in the growth temperature (5). Therefore, measurements of the mechanical properties are expected to be useful for estimating the crystal quality and getting useful information on improvement in the crystal quality.

LaB_6 and CeB_6 crystals are used as an electron source of high brightness and longevity. Improvement in the crystal quality is expected to increase the reliability of electron emission and to decrease the cost of making the emitters. In this report, the crystal quality of LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6, which melt congruently among the rare-earth hexaborides, is estimated from their high-temperature hardness.

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2. EXPERIMENTAL

Commercial powders of LaB_6 and CeB_6 were used as starting materials. The other hexaborides, PrB_6, NdB_6, and SmB_6, were synthesized by heating mixtures of their oxide and boron powders in vacuum according to the following formula:

$$RE\mathrm{O}_x + (6+x)\,B \rightarrow RE\mathrm{B}_6 + x\mathrm{BO}\uparrow,$$

where RE is Pr, Nd, or Sm. After crushing and pulverization of the products, the powder was isostatically pressed (200 MPa) into a rod in a rubber bag and then heated under vacuum at 1700°C for 30 min.

The crystal was prepared at a pressure of 0.5 MPa of an ambient argon gas by the RF heated floating zone method. The growth rate, the lower shaft, was 1 cm/h. Only the growing crystal was rotated at a rate of 6 rpm. The obtained crystals were several mm in diameter and 6 cm long. The details were described elsewhere (1).

Etching patterns were observed under a microscope after a mirror-like polished plane was etched in a HNO_3 aqueous solution (1:3) for several minutes at room temperature.

Microhardness was measured in vacuum from room temperature to 1100°C, using a diamond Vickers indenter (5). The loads were 500 g during 10 s. Hardness was obtained by measuring dimensions of the indentations on the photographs.

3. RESULTS AND DISCUSSION

LaB_6 phase melts congruently at 2715°C, as shown in Fig. 1 (6). The crystals prepared at a congruent composition contained subgrain boundaries, as shown in Fig. 3a. How-

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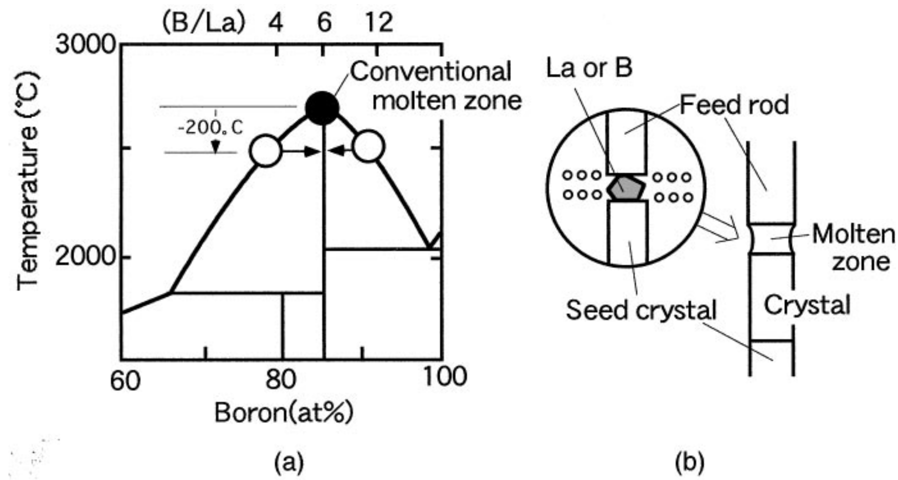

FIG. 1. (a) Phase diagram of the La–B system (6) and (b) the traveling solvent floating zone method by which the high-quality crystals, free of boundaries, are prepared (2, 3).

ever, formation of the boundaries was suppressed when the growth temperature was decreased by 200°C due to controlling the zone composition to La- or B-excessive composition (the traveling solvent floating zone method), as shown in Fig. 1 (2, 3). Therefore, in this report, regarding the LaB_6 crystal growth as a standard that indicates relation between the crystal quality and the hardness, the crystal quality of the other rare-earth hexaborides was estimated from their high-temperature hardness.

Hardness was measured on the (100), (110), and (111) planes of the hexaboride crystals of LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6. The hardness on the (100) planes was measured with good reproducibility because of the clear-cut square shape of the indentations. Therefore, the hardness of the boride crystals was compared on the (100) planes, as shown in Fig. 2. The temperature dependence of the hardness consisted of two linear parts with different slopes in all the samples. In the high temperature range, where the crystal quality is determined due to plastic deformation (4), the hardness of all the hexaborides decreased with the same slope, which suggests that the hexaborides have similar mechanical properties. The hardness of the borides decreased as the atomic number increased. For example, the hardness of LaB_6, CeB_6, PrB_6, NdB_6, and SmB_6 was 1160, 1090, 1080, 1010, and 940 kg/mm^2, respectively, at 900°C. That is, the hardness decreased by 6, 7, 13, and 19%, respectively, compared with that of LaB_6, as shown in Table 1.

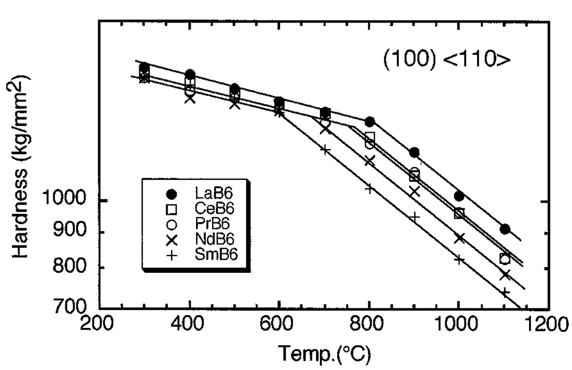

FIG. 2. Vickers hardness on the (100) planes.

On the other hand, their growth temperatures, which were estimated from the heating power (7), decreased as the atomic number increased, as shown in Table 1. Their growth temperatures decreased by 140, 210, 250, and 370°C, respectively, compared with the LaB_6 crystal growth at a congruent-melting composition, 2715°C (6). The decrease in the growth temperature corresponds to an increase in the hardness by 19, 30, 37, and 60% in the cases of CeB_6, PrB_6, NdB_6, and SmB_6, respectively, as estimated from the temperature dependence of the hardness in Fig. 2.

Therefore, the crystals of CeB_6, PrB_6, NdB_6, and SmB_6 were estimated to have higher hardness by 10% (= 19–9), 20% (= 30–10), 23% (= 37–14), and 41% (= 60–19), respectively, at their growth temperatures, compared with that of LaB_6 crystals prepared at a congruent composition, as shown in Table 1. In the case of the LaB_6 crystal, the decrease in the growth temperature by 200°C leads to an increase in hardness by 28% and the disappearance of subgrain boundaries (2, 3). Therefore, the quality of CeB_6 crystals are expected to be a little better than that of the LaB_6 crystals, but the PrB_6 and SmB_6 crystals are expected to be of much better quality.

Figure 3 shows the etching patterns of the (100) planes. The crystal quality increased as the atomic number of the rare-earth metal increased. LaB_6 crystals prepared at a congruent composition had many subgrain boundaries, demonstrated as lines in Fig. 3a. The CeB_6 crystal contained

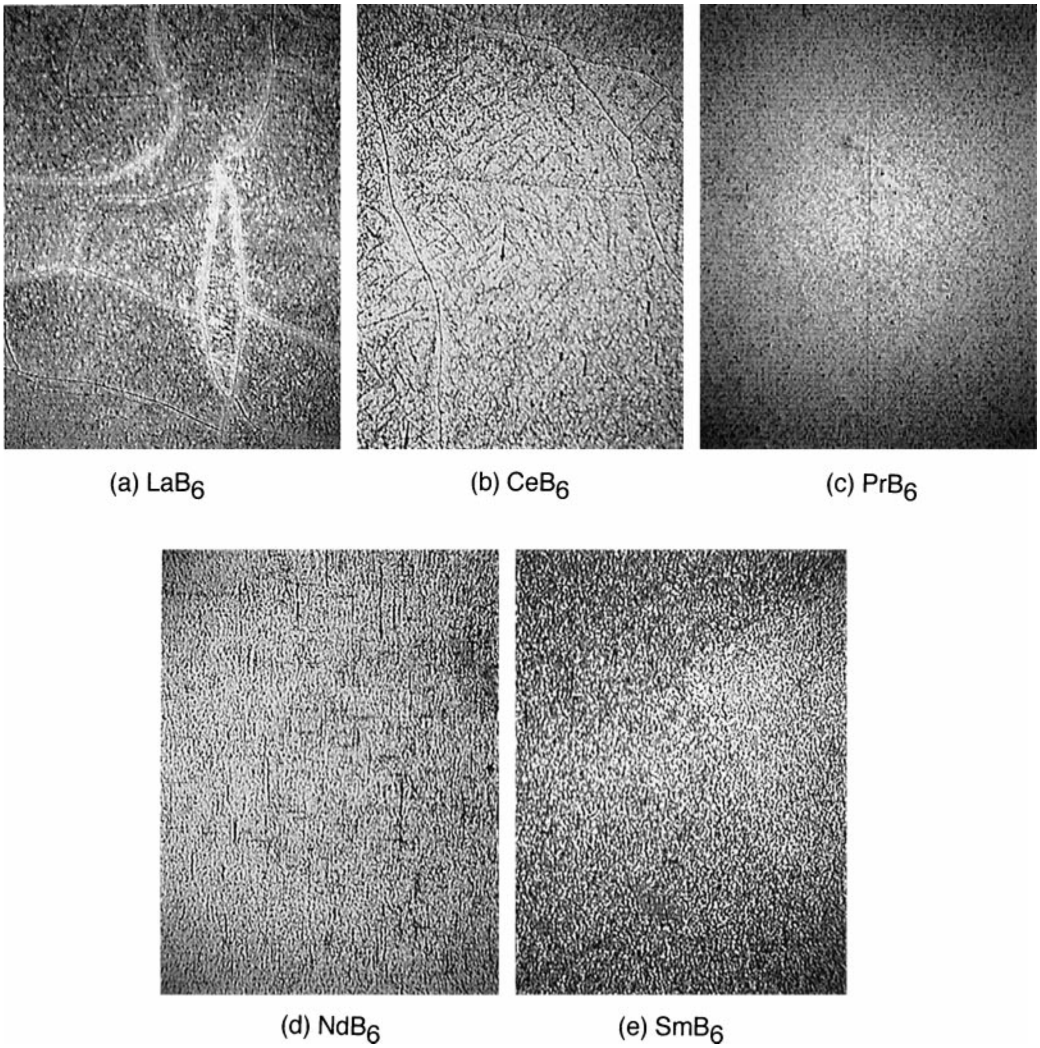

FIG. 3. Etching patterns of the (100) planes of (a) LaB_6, (b) CeB_6, (c) PrB_6, (d) NdB_6, and (e) SmB_6 crystals. The size of the photographed area is 4×3 mm.

fewer boundaries than the LaB_6 crystal. Few boundaries were contained in the PrB_6, NdB_6 and SmB_6 crystals. Therefore, the crystal quality of the hexaborides was well consistent with the estimation from the hardness.

4. SUMMARY

The crystal quality of the rare-earth hexaborides was estimated from the high-temperature hardness and the

TABLE 1
Growth Temperature and Vickers Hardness

	Growth temp.		Hardness (kg/mm^2)			Increase in hardness at the growth temperature (%)
	°C	ΔT	ΔH^a (%)	(at 900°C)	ΔH^b (%)	
LaB_6	2715	(0)		(1160)		
(boundary-free)	2515	(− 200)	+ 28	(1160)	0	+ 28
CeB_6	2575	(− 140)	+ 19	(1090)	− 6	+ 13
PrB_6	2505	(− 210)	+ 30	(1080)	− 7	+ 23
NdB_6	2465	(− 250)	+ 37	(1010)	− 13	+ 24
SmB_6	2345	(− 370)	+ 60	(940)	− 19	+ 41

[a] Increase in hardness estimated from decrease in the growth temperature (see Fig. 2).
[b] Decrease in hardness of the borides, compared with LaB_6 (see Fig. 2).

growth temperature. The hardness at their growth temperature was well consistent with the crystal quality. The hardness measurement, a simple method of examining mechanical properties, was found to be useful for estimating crystal quality in the case of a series of structurally similar compounds.

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