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On the Growth and Properties of Single Crystal LaB_4

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A technique has been developed for the growth of single crystals of lanthanum tetraboride LaB_4, from solution in La. Under optimum conditions, crystal size is limited by the size of the crucible. Lattice parameters, thermal expansion coefficient, and microhardness are reported and the growth facets have been identified. An initial check on the electron emitting properties have shown them to be comparable with those of LaB_6.

1. Introduction

The borides of the Group IIIA elements (Sc, Y, La, and the rare earth metals) have been examined several times [1-4] since Lafferty showed in 1951 that the IIIA hexaborides, and LaB_6 in particular, showed great promise as electron emitters [5]. Most effort has gone into LaB_6 but this has not so far led to the production of large single crystals. The reported melting point of $> 2500°C$ for LaB_6 has perhaps discouraged the application of conventional melt growth techniques. Polycrystalline LaB_6 rods for electron emitters have been produced by hot sintering of powders and by arc melting and both have been found to have similar properties [6]. Electron emitters of polycrystalline material do, however, show some defects. For example, there are variations in resistivity and thermal conductivity due to grain boundary effects and the orientation of the small grain which happens to form the emitting point cannot be controlled. There is also a tendency for the emitting point grain to fall out in use.

The Group IIIA tetraborides are less well known than their hexaborides and have for the most part only been studied with respect to their crystallographic and chemical properties [7]. In few cases are the relevant phase diagrams known but the La-B system has been partially determined [3, 8] and is shown in fig. 1. It may be seen that LaB_4 is a peritectic compound decomposing to LaB_6 + La at about 1800°C. It is in equilibrium with metallic La at all temperatures.

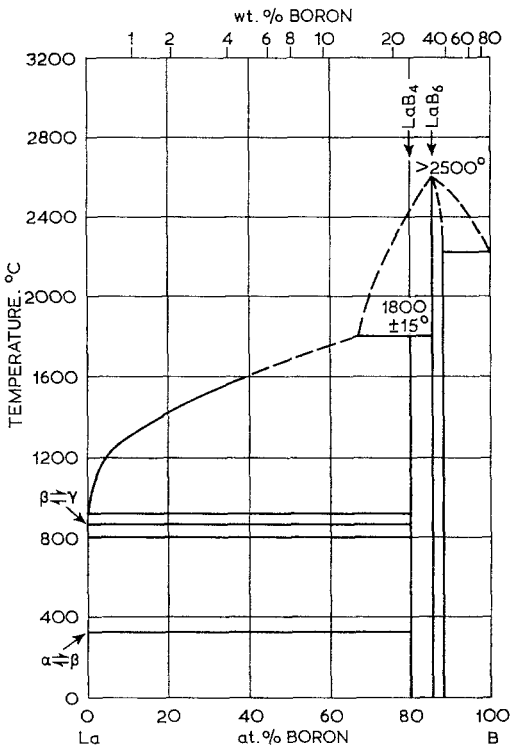

Figure 1 The equilibrium diagram of the B-La system after Johnson and Daane.

1.1 Growth of LaB_4

It appears from fig. 1 that while LaB_6 could be grown from the melt if sufficiently high temperatures could be obtained, LaB_4 cannot be

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produced from a melt of its own composition. A less direct method for the growth of LaB_4 must therefore be used and the most obvious is the controlled cooling of a solution of LaB_4 in La in the temperature range 1780 to $\sim 1300°C$. This must give rise to crystals of LaB_4 in a matrix of La which can easily be etched away. In principle LaB_6 could also be grown from La solution between the melting point and 1800°C, but in this case it would be necessary to separate the LaB_6 product from a matrix containing large amounts of LaB_4 which is difficult to separate being chemically as inert as LaB_6. Similar difficulties would attend the growth of LaB_6 from Boron solution.

2. Experimental

For convenience an RRE crystal puller incorporating a 100 mm diameter silica tube with a side-arm was used in conjunction with a 15 kW, 450 kc induction heater, as a high temperature furnace. The side-arm was fitted with an optical window of silica for observation and optical pyrometry and the chamber was fitted with gas and vacuum lines and a pressure gauge.

Crucible materials tend to present a problem when dealing with the Group IIIA metals. Magnesia, reported to be stable to rare earth metals, was attacked quite rapidly by molten La but Ta was found to be quite stable. Crucibles of 19 mm diameter and 24 mm height were therefore drawn from 0.14 mm Ta sheet and found to be satisfactory. Lids, with a small hole for pyrometer sighting were cut from sheet Ta with projecting tabs, so that they could be spot-welded in place.

A graphite susceptor, fitted with a perforated lid contained the crucible and was separated from the crucible, to prevent the formation of TaC, by an alumina tube and a magnesia disk. The susceptor and contents were in turn contained in a magnesia chamber which was again perforated for optical pyrometry. The whole assembly, shown schematically in fig. 2, was supported on a graphite rod in the puller chamber.

The boron, with a quoted purity of 99.5%, was in the form of a coarse powder and was supplied by Koch-Light Ltd. The lanthanum, with a quoted purity of 99.9%, was supplied in the form of a single lump by Rare Earth Products Ltd.

Lanthanum pieces of suitable size were cut with a hack-saw, degreased, filed clean, and weighed. The weight of boron to yield a 40 at. % Boron in Lanthanum mixture was then calculated and weighed out. These were placed in the crucible with the lanthanum on top and the lid was spot-welded in place.

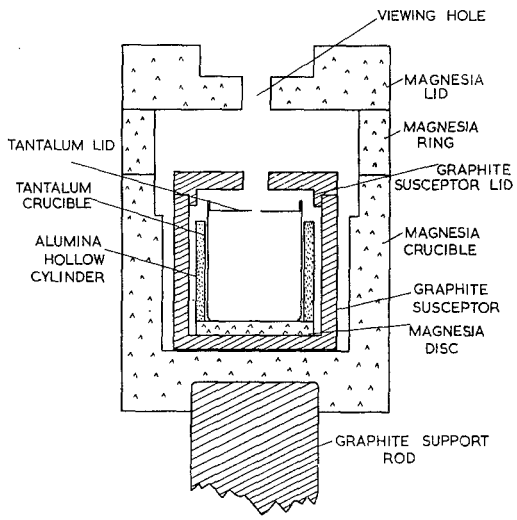

Figure 2 Schematic representation of the crucible, susceptor and insulator arrangement.

The growth procedure was as follows. The entire system was assembled without the Ta crucible and contents, and was flushed four times with high purity argon. It was then baked out under vacuum for about 30 min at 1600°C to remove moisture and other volatile impurities. On cooling, the system was broken down, the crucible and contents inserted and the whole reassembled and again flushed out four times with argon with the minimum of exposure to atmosphere.

The temperature was now raised to and equilibrated at about 1700°C, after which it was steadily lowered, to about 1250°C, by means of a motorised potentiometer in the RF feedback loop. The cooling rate was not quite linear, but averaged 16°C/h between 1600 and 1250°C. The furnace was then switched off and allowed to cool.

Temperatures were measured throughout by means of an optical pyrometer sighted through the holes in the crucible and insulator assembly. To standardise the pyrometer three standards, Si (1412°C), Ni (1453°C), and Pt (1769°C) were used in the same crucible assembly as above. In each case a thin alumina rod supported by the standard within the crucible, and projecting

through the sighting holes so as to be visible from outside the assembly, dropped when the standards melted, at which point the corresponding pyrometer temperature was noted. All temperatures quoted have been corrected according to the calibration line thus obtained.

When cool, the crucible was removed from the furnace and its lid was removed. The crucible and contents were placed in 150 ml of 1:1 HCl. A vigorous reaction took place between the HCl and La with the evolution of hydrogen. The temperature of the reactants reached about 60°C.

Figure 3 Crystals of LaB_4 produced in Run 11.

After 16 h of such etching the Ta crucible with the crystals within it was removed from the acid and examined. Single crystals of LaB_4, confirmed later by X-ray analysis, were found. The crystals were washed in distilled water until no trace of HCl remained.

Crystals of LaB_4 were well faceted and metallic in appearance. They could be etched with concentrated H_2SO_4. Crystals varied in size from small granules at fast growth rates to a crystal (fig. 3) limited only by the diameter of the crucible. The majority of the good crystals were in the 5 to 8 mm range (fig. 4).

3. Evaluation

Using the Debye-Scherrer X-ray technique a powder sample of LaB_4 was examined in a 57.3 mm radius camera with nickel filtered copper radiation (CuK_α = 1.5418 Å). No lines were present which could not be attributed to LaB_4 on the basis of the reported structure and lattice parameters [3]. Visually the line intensities showed LaB_4 to be isomorphous with UB_4 [9].

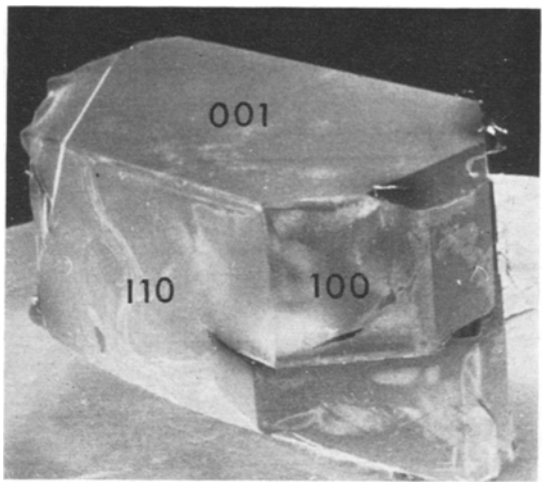

Figure 4 Crystal of LaB_4 showing typical growth facets. The crystal is 5.5 mm long.

Using Laue patterns the three main facets of a typical LaB_4 crystal (fig. 4) were examined. From symmetry and indexing of spots the growth facets were shown to be {001}, {110} and {100}, the order of these faces giving areas in decreasing magnitude. For the isostructural compound ThB_4 [9] the crystal faces were of the forms {001} and {110}. By X-ray diffractometer, lattice parameters were found to be $a = 7.32462 \pm 0.00003$ Å and $c = 4.18091 \pm 0.00002$ Å at 20°C. No correction for refraction was made. A plot of temperature versus lattice parameter c gave a coefficient of linear thermal expansion of 4×10^{-6}/°C. Because of the uncertainty of temperature, this is not a precise figure.

The Reichert Micro-Hardness Tester [10] was used on the {001} face of a single crystal with dimensions 5 × 3 mm. The microhardness of the LaB_4 crystal on the {001} face was found to be 2190 kg/mm² for an indentation load of 50 g. The Meyer exponent n was calculated to be 1.85 indicating the microhardness dependent on load case. The resistivity of an LaB_4 crystal was found to be $22 \pm 4.4 \times 10^{-6}$ ohm-cm at 19°C.

In view of the very good electron emitting properties of LaB_6 [6] a 1 mm square section of LaB_4 was cut from a single crystal, using a wire saw, pointed by grinding, attached to a similar sized rod of LaB_6 and mounted in an electron gun. Qualitative results showed LaB_4 to have very similar emitting properties to the LaB_6. It was noted at the end of the test run that a bluish colouration occurred at the tip of the emitter.

This may have been due to LaB_4 being converted to the more stable boride LaB_6 [3]. An analysis of the tip material was not performed.

4. Conclusions

It has been demonstrated that sizeable crystals of LaB_4 may be grown from La solution and that, when conditions are right, the maximum crystal size is limited by the size of the crucible. There is every reason to believe that larger crystals could be produced if required by a suitable scaling up. Accurate lattice parameters and an approximate coefficient of thermal expansion have been determined and the pronounced growth facets have been identified by X-ray techniques. The microhardness on one facet has been tested and an approximate electrical resistivity determined.

Initial tests have shown the performance of LaB_4 as an electron emitter to be comparable with that of LaB_6. It has been reported [3] that LaB_4 converts to LaB_6 by vapour loss of La. There was in fact a faint bluish tinge, reminiscent of the usual LaB_6 surface, on the tip of the LaB_4 sample after testing and it seems possible that conversion at the surface had taken place. If this is so, then the production of electron emitters from LaB_4 single crystals may be a technique for obtaining what amount to LaB_6 single crystal emitters, which have not hitherto been available. Further work is required to confirm that this change does in fact occur and, if it does, how quickly it occurs and how deep into the crystal the effect goes. One would also wish to know if this change is single crystal LaB_4 to single crystal LaB_6 and, if so, what the orientation relationships are.

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