Armstrong [14] has suggested that at intermediate stress (σ) levels and at high temperatures, superplastic behaviour of fine grain sized materials is a result of the pronounced temperature dependence of the self diffusion coefficient (D) in the following equation

$$\dot{\epsilon}_{\mathrm{mcr}} = \left[\frac{10\Omega D\sigma}{RT}\right] d^{-2} \qquad (2)$$

where Ω is the atomic volume and d the grain size. The present set of results indicate that superplastic behaviour occurs at intermediate temperatures 0.5 T_{m} (T_{m} is the melting temperature in degrees absolute) and at fast strain-rates 3.94×10^{-2} min^{-1}, which suggests that the grain-size weakening effect is not explicitly dependent on the self diffusion coefficient. A more likely source for this effect is the marked increase in grain boundary sliding with a decrease in grain size.

In conclusion it has been shown for this alloy that:

(i) the room temperature strength can be increased by a decrease in grain size,

(ii) the minimum creep rate can be decreased by an increase in grain size and

(iii) that superplastic deformation occurs at 0.5 T_{m} at a strain-rate of 3.94×10^{-2} min^{-1} and a 1 % flow stress of 24 MN m^{-2} in 1 μm grain sized material which exhibits high room temperature strength.

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R. G. FLECK
Department of Physical Metallurgy
and Science of Materials,
University of Birmingham,
Birmingham, UK

D. M. R. TAPLIN
Department of Mechanical Engineering,
University of Waterloo,
Ontario, Canada

Flux growth of the rare earth borates, RBO_3

Single crystals of the aragonite and calcite type RBO_3 compounds have been prepared. With R = Sm to Yb, it appears that the high temperature vaterite structure transforms to a room-temperature structure of lower symmetry. Hexagonal pseudomorphs with this structure were flux-grown by the slow cooling method.

The rare earth borates, RBO_3, fall into three groups according to their crystal structure, each group being structurally related to one of the three forms of calcium carbonate. At room temperature, those with R = La to Nd have the orthorhombic structure of aragonite [1-3]. Those with R = Sm to Yb have a structure which resembles that of vaterite, but Levin *et al* remark that these are really pseudo-hexagonal, as it was not possible to index all the lines on the X-ray powder pattern [1]. The divergence from the vaterite structure has been confirmed by studies of vibrational spectra [4-6]. Below 1310°C,

TABLE I Composition and growth conditions for RBO_3

R	Components	Crucible volume	Max. temperature (°C), and soak period	Cooling rate and minimum temp. (°C)	Result
La	7.3 g La_2O_3, 8 g B_2O_3, 80 g PbO, 2 g PbO_2	50 ml	1270°, 7 h	5.5°/h to 700°	Transparent platelets up to (10 × 4) mm^2 and rods (5 × 1 × 1) mm^3
Pr	6.6 g Pr_4O_7, 8 g B_2O_3, 8.6 g MoO_3, 80 g PbO, 2 g PbO_2	50 ml	1280°, 5 h	6°/h to 800°	Transparent green rods up to (8 × 0.7 × 0.5) mm^3
Nd	5 g Nd_2O_3, 12.8 g B_2O_3, 13.8 g MoO_3, 128 g PbO, 1 g PbO_2	50 ml	1270°, 1 h (growth below 1000°C)	4.5/h to 800°	Transparent purple rods
Er	3.8 g Er_2O_3, 4.3 g MoO_3, 40 g PbO, 4 g B_2O_3	40 ml	1250°, 2 h	6°/h to 800°	Translucent pink plates, hexagonal, 8 mm across
Lu	1 g Lu_2O_3, 0.3 g B_2O_3, 2.4 g PbO, 18 g PbF_2, 0.2 g PbO_2	10 ml	1260°, 20 h	1°/h to 1150°	Single transparent, colourless crystals, 5 mm on edge.

$LuBO_3$ has the monoclinic calcite structure [1].

The growth of RBO_3 single crystals has not been reported, but references have been made to its appearance as an unwanted phase during the flux growth of other rare earth compounds from PbO-B_2O_3 [7] and from PbO-PbF_2-B_2O_3 [8]. The melting point of $DyBO_3$ is given as 1670 ± 10°C [9].

Crystal growth experiments were carried out using platinum crucibles with closely-fitting lids. After an initial "soak" period, the melts were either slowly cooled or held at a high temperature to evaporate the flux.

The crucibles, furnaces and control equipment have been previously described [10]. The chemicals used were: Rare Earth Products 99.9% R_2O_3, BDH "Analar" grade PbO and PbO_2, BDH "Optran" PbF_2, and BDH Laboratory reagent grade B_2O_3. Crystals were identified by comparison of their X-ray powder patterns with published data [11]. Table I lists the components, growth conditions and results.

Rare earth borates with the orthorhombic aragonite structure RBO_3 (R = La to Nd). Suitable fluxes for $LaBO_3$ were found to be PbO-B_2O_3 and PbO-B_2O_3-MoO_3.

$LaBO_3$ and $NdBO_3$ undergo phase transformations at 1490 and 1090°C respectively [1], and by interpolation from a graph of ionic radius of the rare earth ion against transformation temperature, $PrBO_3$ probably undergoes a crystallographic transition near 1220°C. Thus, to obtain $PrBO_3$ and $NdBO_3$ as untwinned crystals, the solute concentration was reduced so that growth should commence below their respective transition temperatures.

$LaBO_3$ crystals grew mainly as transparent platelets as shown in Fig. 1. $PrBO_3$ and $NdBO_3$ crystals were largely transparent green and purple rods respectively. Fig. 2 shows untwinned crystals of $PrBO_3$ growing at the surface of the melt. The crystals were mechanically separated from the flux and cleaned briefly in hot, dilute HNO_3. Prolonged immersion resulted in their dissolution.

The lead content of the $PrBO_3$ crystals was found to be 0.36%.

Rare earth borates with a pseudo-hexagonal

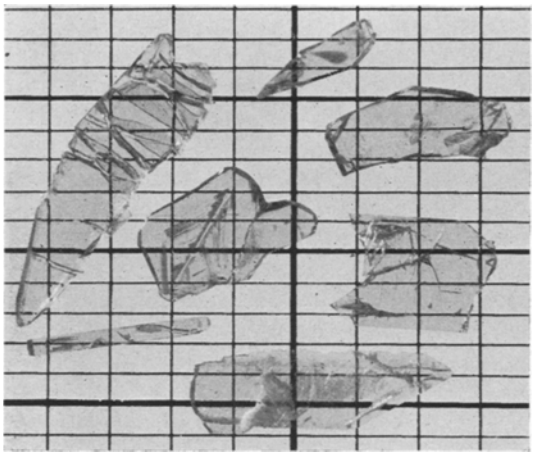

Figure 1 Platelets of $LaBO_3$ (1 × 2 mm divisions).

structure resembling that of vaterite (R = *Sm to Yb, and Y*). $DyBO_3$, $HoBO_3$ and $ErBO_3$ crystals were obtained from the flux mixtures found suitable for $LaBO_3$ in the form of large plates 8 mm wide, which nucleated and grew both on the melt surface and at the crucible base. The plates had typical hexagonal outlines but it was concluded that they were pseudomorphs, as they were highly twinned and nearly opaque. Thus, although no inversions have been observed in YBO_3 at temperatures below 1000° C by differential thermal analysis [1], it is evident that a crystallographic transition does occur below the growth temperature.

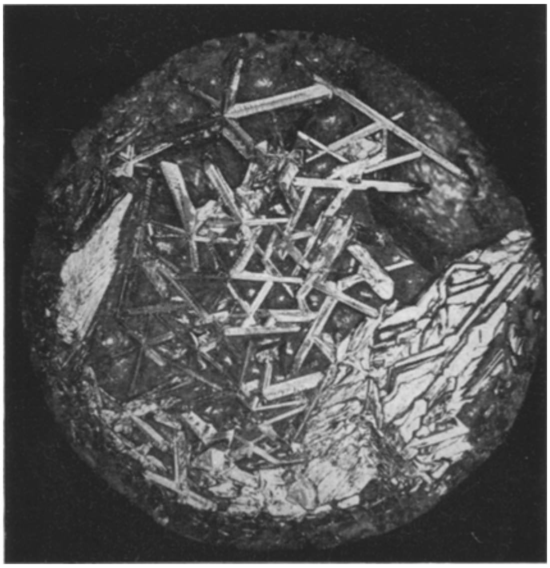

Figure 2 $PrBO_3$ rods and platelets at the surface of the melt (× 2.5).

In an attempt to grow crystals below the transition temperatures, more dilute batches were used, but hexagonal pseudomorphs always resulted.

$LuBO_3$, with the monoclinic calcite structure. Attempts to grow $LuBO_3$ by slow cooling, using the fluxes found suitable for $LaBO_3$, produced only highly twinned platelets with the vaterite type structure. Transparent, colourless single crystals were obtained, however, by using PbF_2 as flux, and allowing it to evaporate while cooling from 1260 to 1160° C.

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BARBARA M. WANKLYN
Clarendon Laboratory,
Dept. of Physics,
University of Oxford, UK