

Stimulated by these results, a new gradient furnace has been built. Its main characteristic is that the heat flow is transverse to fibres in dovetail-shaped samples. The temperature distribution is symmetrical and the temperature is carefully controlled. Details are to be published elsewhere [3].

A Co-17% Cr-10% NiTaC eutectic was directionally solidified at a rate of 0.6 cm h⁻¹. 5 mm diameter specimens were annealed in a temperature gradient of 270 K mm⁻¹ in a vacuum in excess of 10⁻¹ Pa. After 250h annealing no change in microstructure was detected, and no increase in the fibre diameter or spacing or any change in fibre shape were observed (Fig. 1).

It is concluded, therefore, that under the above-mentioned test conditions there is no visible

coarsening or fibre degradation in this eutectic system.

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Flux growth of lanthanum borate, LaBO₃

The rare earth borates, RBO₃, fall into three groups according to their crystal structure, each group being structurally related to one of the three forms of calcite. LaBO₃ has the orthorhombic structure of aragonite and is pseudo-

hexagonal, with the pseudo-hexagonal *c*-axis parallel to the orthorhombic *b*-axis [1-3].

It has been shown that LaBO₃ can be grown from PbO-B₂O₃ in the form of small rods or platy crystals [4]. Recently, a model has been proposed for the prediction of starting compositions for the flux growth of crystals with one

TABLE I Compositions and growth conditons for LaBO₃

Starting composition* (mol%) (dry materials)			Crucible volume (ml)	Max. temperature and soak period		Cooling rate and minimum temp.		Notes on the results
La ₂ O ₃	B ₂ O ₃	PbO		°C	h	°C h ⁻¹	to °C	
4.0	40	56.0	10	1250	15	3	700	Many small transparent platelets grew in a layer at the surface
3.7	12	84.3	10	1250	15	3	700	Large transparent platy crystals, up to 10 mm × 3 mm × 1 mm, at the melt surface only
4.3	13.2	82.5	10	1250	15	3	700	All crystals grew at the base of the crucible. Rods up to 3 mm × 1.5 mm × 1 mm, tabular crystals up to 4 mm × 3 mm × 1 mm and equi-dimensional crystals 2 mm on edge
4.6	13.2	82.2	10	1250	15	3	700	Rods up to 4 mm × 1.5 mm × 1 mm and faceted crystals 3 mm × 2 mm × 2 mm grew at the crucible base. Solution was complete
5.0	13.1	81.9	10	1250	15	3	700	Many intergrown crystals, indicating that solution was not complete

*Several batches of each composition were prepared.

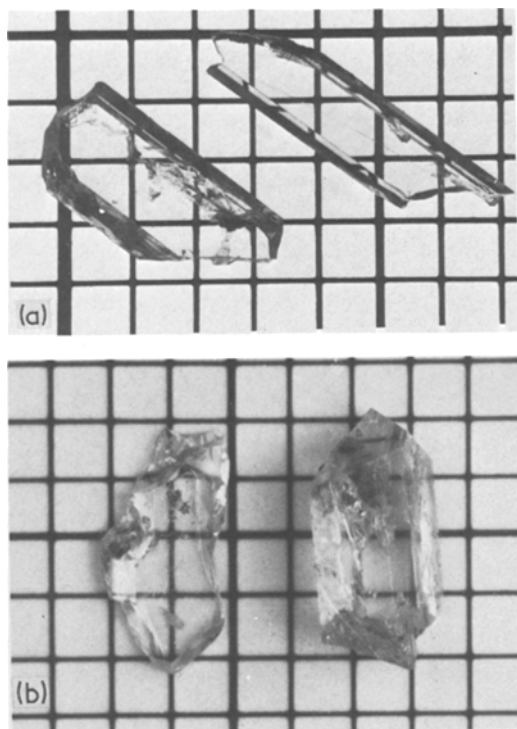


Figure 1 (a) Platelets of LaBO_3 (1 mm grid) (b) Tabular prisms of LaBO_3 (1 mm grid) (c) Approximately equi-dimensional crystals of LaBO_3 (1 mm grid).

refractory and one relatively low-melting component (such as La_2O_3 and B_2O_3 , respectively) from fluxed melts [5]. According to this model, increasing the proportion of basic oxide relative to acidic oxide may be expected to result in more equi-dimensional, fewer and larger crystals. This letter describes such experiments in the system La_2O_3 - PbO - B_2O_3 and experiments in which the proportion of La_2O_3 was varied.

The chemicals used were: 99.99% pure La_2O_3 from Rare Earth Products, BDH "Analar" grade PbO and BDH Laboratory Reagent grade B_2O_3 . The La_2O_3 and B_2O_3 were calcined at 1000 and 700°C, respectively, prior to use.

Many experiments were performed, and Table I reports representative starting compositions, furnace programmes and results. In all cases, the furnace gradient was such that the crucible base was a few degrees cooler than its upper parts.

As the proportion of PbO was increased from 56% to over 80%, the number of crystals decreased from a large number to a few only. With 56% PbO , there were over 50 small platelets about 0.1 mm thick at the melt surface. With over 80% PbO , however, only a few larger plates, up to

2 mm thick, were obtained from a 50 cm³ crucible. These results are in accord with previous studies in such ternary systems [5, 6].

In other experiments, the concentration of PbO was kept at 80 to 85% while the concentration of La_2O_3 was increased from 3.7 to 5%. Complete solution was obtained at 1250°C for a concentration of 4.6%, and few crystals grew, but at 5% it was evident that solution was incomplete. With 3.7% La_2O_3 , only plates of LaBO_3 at the surface were obtained, but with 4.3 and 4.6% La_2O_3 , crystals of very different habit grew at the base or lower walls of the crucible. The latter crystals were in the form of (1) tabular prisms (2) rods and (3) approximately equi-dimensional crystals, as illustrated in Fig. 1. The major faces developed in each type were studied by optical and X-ray techniques. The study showed that the major faces of the platelets are (100), the long directions being the *c*-axis. The tabular prisms have (100) and (110) faces, with the long direction again the *c*-axis. The rod-shaped crystals have larger (120) faces, and are also elongated in the *c*-direction, with four relatively small facets at each end. The equi-

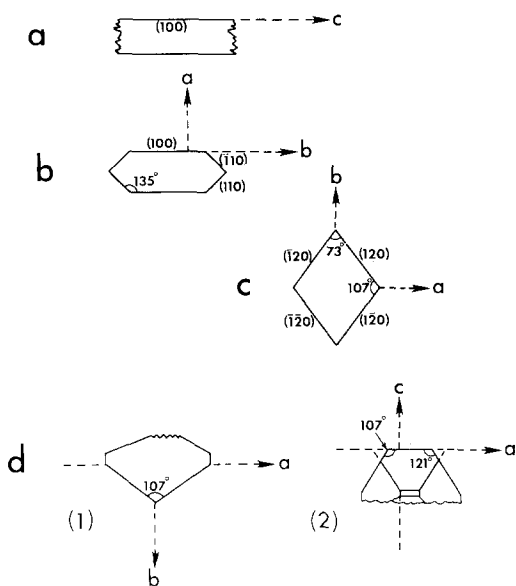


Figure 2 (a) Platelet. The major faces are (100), the long direction is the *c*-axis. (b) Tabular prism in cross-section, seen along the *c*-axis. (c) Cross-section, viewed along *c*-axis, of a rod. (d) Approximately equi-dimensional crystals (1) viewed along the *c*-axis (*a* > *c*). (2) viewed along the *b*-axis, indicating complex morphology.

dimensional crystals show a complex morphology having as many as twenty facets. Fig. 2 shows schematic diagrams in which some of the facets are identified.

Flux growth with relatively high concentrations of refractory oxide and, therefore, at relatively high temperatures, usually favours more equi-dimensional crystals, as has been noted with Cr₂O₃, Al₂O₃, Fe₂O₃, NiTiO₃, and garnets [7].

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Changes in habit similar to those reported here, platy at the melt surface and more equi-dimensional within the melt, have been reported for flux grown MgO, Al₂O₃, FeVO₄, ZnO, CeO₂ and TiO₂ [7].

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Electrical conduction in 'pure' and copper-doped KHSO₄

Electrical conduction in hydrogen-bonded materials such as KH₂PO₄, NH₄H₂PO₄ (both undoped and doped with Ba²⁺, HSO₄⁻ and SO₄²⁻ ions), and (NH₄)₂SO₄:HSO₄⁻ has been demonstrated to be protonic from coulometric determination of transport numbers, electrical conductivity measurements and NMR of deuterated samples [1-5]. Quite recently, KHSO₄ was shown to be a protonic conductor from d.c. electrolysis experiments on

Co-doped KHSO₄ crystals and the transport number of protons was found to be nearly unity [6]. We report in this letter, d.c. electrical conductivity results on 'pure' (undoped) and copper-doped KHSO₄ single crystals, in the range 50 to 180 C, the upper temperature limit being dictated by the rather low decomposition temperature (~210 C) of this hydrogen-bonded system. This study was motivated by our earlier work on the ESR of Cu²⁺ impurity in KHSO₄ crystals [7], where we had postulated that both K⁺ and proton vacancies exist in KHSO₄ and that both types