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The composition of crystals of bismuth silicon oxide

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Crystals of $Bi_xSiO_{1.5x+2}$ with $x \sim 12$ can be pulled at rates of about 5 mm h^{-1} from platinum crucibles in oxidizing atmospheres. Melts with x in the range $10 < x < 15$ give crystals in which the range of x is only from $x = 11.77 \pm 0.03$ to $x = 12.05 \pm 0.10$. As a function of melt composition, the solid composition shows a minimum and a maximum. Growth from melts giving either extreme, results in crystals having a constant composition.

1. Introduction

Bismuth oxide can be stabilized in the cubic γ-form (space group I23 [1]) by the addition of small amounts of the oxides of Ga, In, Zn, Fe, Ge or Si [2, 3]. These materials have interesting electro-optic and piezo-electric properties. This paper describes an investigation into the composition of pulled crystals of the silicon stabilized material which has the approximate formula $Bi_{12}SiO_{20}$ but which is better described as $Bi_xSiO_{1.5x+2}$.

2. Experimental

Differential thermal analysis confirmed that $Bi_{12}SiO_{20}$ melts congruently at 895 ± 5° C, so that the Czochralski method of growth [4] may be used. Crystals were pulled at rates of up to 8 mm h^{-1} from platinum crucibles 35 mm diameter, 32 mm deep with a wall thickness of 1 mm, contained in a stainless steel chamber attached to a hydropneumatic crystal puller [5]. No afterheater was used. Radio frequency power at about 350 kHz was provided by an Intertherm 30 kW generator and the output power was stabilized by a Philips 1653 grid current controller. This system could keep the crucible temperature constant to within 0.2° C.

The melts were prepared by fusing together appropriate mixtures of Bi_2O_3 and SiO_2 (both materials were Johnson Matthey grade 1). The crystals were pulled in atmospheres of either oxygen or air, initially using a piece of platinum wire as a seed and later using seeds cut in ⟨111⟩, ⟨110⟩ and ⟨100⟩ directions from previously grown boules.

The compositions of the crystals and the melts were determined colorimetrically. For bismuth, the thiourea complex was used and for silicon the yellow molybdo-silicic acid complex was employed. The analyses gave x in $Bi_xSiO_{1.5x+2}$ with a reproducibility of ± 0.1 for $10 < x < 15$. (A small platinum crucible was used to sample the melts at the beginning and end of the growth period and corresponding solid samples were taken from the top and bottom of the boules.) The analyses of melts at the commencement of growth agreed within this limit with the value of x expected from the weights of the previously baked reagents. Note that Bi_2O_3 absorbs CO_2 to form bismutite $Bi_2O_3 \cdot CO_2$ [6] and this could change the apparent bismuth content in unbaked samples by as much as 1.5%, although a more typical change was 0.3%. In order to eliminate variations from this source each batch of starting material was analysed immediately before use.

3. Results and discussion

Crystals up to 20 mm diameter could be pulled and it proved possible to grow out all but about 5 g of the 150 g charge. However, it was easier to grow crystals about 12 mm diameter and we generally only used about half the charge in each experiment. For values of x in the melt near to 12 inclusion-free crystals could be grown provided that the growth rate was always less than 6 mm h^{-1} and the diameter was not allowed to decrease rapidly. (If the diameter decreased sharply, inclusions formed in the centre of the crystal and persisted for several millimetres after a constant diameter was re-established.) For crystals with diameters over 15 mm and for x in the melt significantly different from 12, lower growth rates were used (4 to 5 mm h^{-1}).

Crystals were grown on $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ axes. Facets corresponding to $\{110\}$ faces were formed in all cases and sometimes $\{100\}$ facets were also found. The material grown on the facets was appreciably darker than the rest of the crystal but mass spectrometric analysis revealed no significant difference in impurity content and the ratio of bismuth to silicon did not differ significantly (i.e. the values of x differed by less than 0.1).

Rotation rates up to 70 rpm were used but there appeared to be no advantage in using a high rate, so that most of the crystals were grown with a rotation rate of 45 rpm.

TABLE I

Compositions		Lattice constant
Melt (x_L)	Crystal (x_S)	(a_0 − 10.1000) × 10^4
10.6	11.90 ± 0.07	33 ± 3*
11.5	11.85 ± 0.03	30 ± 3
11.7	11.77 ± 0.03	30 ± 1
12.1	11.92 ± 0.04	31 ± 2
12.8	12.03 ± 0.06	32 ± 4
13.3	12.05 ± 0.10	33 ± 4
14.4	12.03 ± 0.03	32 ± 1

*The lattice constant for crystal grown from melt x_L = 10.6 is 10.1033 ± 0.0003 Å.

Table I and Fig. 1a give X-ray and compositional data for crystals grown from melts with $10 < x_L < 15$. The values given are averages from several experiments. The change in composition (Δx_S) between the top and bottom of a crystal was measured. Fig. 1b gives these data for a series of 50 g crystals grown from 150 g melts. Note that the change in solid composition should be roughly proportional to the slope of the curve in Fig. 1a and the curves in Fig. 1a and b have been adjusted to fulfil this condition.

From these data, it seems that we can grow constant composition crystals at either the maximum or minimum value of x_S and presumably these compositions correspond to the maximum limits of solid solubility for excess of either component.

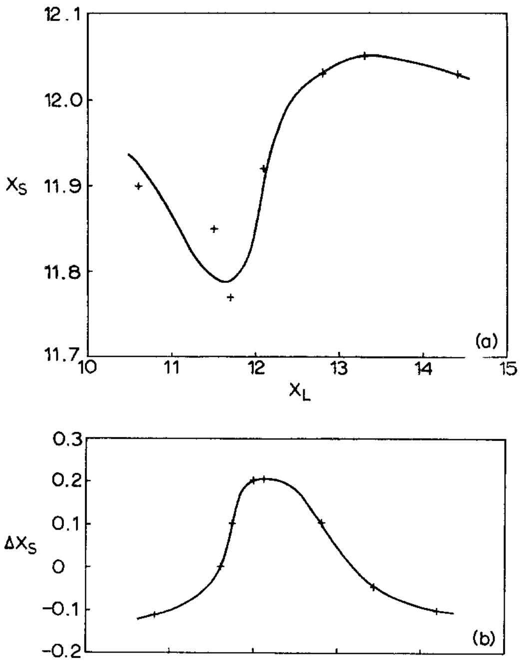

Figure 1 (a) The variation of solid composition (x_S) with melt composition (x_L). (b) The change in solid composition (Δx_S) which occurs after one third of the melt is used up as a function of the initial composition of the melt.

4. Conclusions

This investigation has defined the conditions under which small crystals of γ-Bi_2O_3 stabilized with silicon may be grown and has shown that the composition of the crystals is a function of melt composition which shows both a minimum and a maximum. Growth from a melt giving either extremum results in crystals with essentially constant composition.

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