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Stability Regions for the Growth of Barium-Strontium Niobate Crystals

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Crystals of barium–strontium niobate solid solutions can be grown from fluxes consisting of mixtures of barium and strontium tetraborate. The ferroelectric (tetragonal) form of the solid solutions is found to be metastable at temperatures below about 850°C, the stable structures being $BaNb_2O_6$ (pseudohexagonal) and strontium niobate (orthorhombic). Partial phase diagrams are given for the BaO–B_2O_3–Nb_2O_5 and the $BaNb_2O_6$–$SrNb_2O_6$ systems.

1. Introduction

The barium–strontium niobate solid solutions $Ba_xSr_{1-x}Nb_2O_6$, with ferroelectric tetragonal-bronze structure, are known to be very low-voltage electro-optic materials (*1*, *2*) and, as such, have attracted considerable attention during recent years. Papers have been published describing the growth of barium–strontium niobate by pulling from the melt (*2*, *3*) and this paper describes work done on the crystallization of these solid solutions from a high-temperature flux.

2. Phase Equilibrium Studies

Carruthers and Grasso (*4*) have recently published a phase diagram describing the (barium niobate)–(strontium niobate) system. There does not appear to be any published work describing systems between barium–strontium niobate solid solutions and another compound, although a paper has appeared which described the crystallization of barium niobate from barium diborate flux (*5*). Preliminary crystal growth runs were, therefore, carried out using mixtures of barium oxide, strontium oxide and boron oxide as possible solvents for the barium–strontium niobate.

The method used for the crystal growth runs was as follows: Weighed amounts of barium carbonate, strontium carbonate, niobium pentoxide, and boric acid (all Specpure grade from Johnson–Matthey) were mixed and sintered at 1000°C in a 35 ml platinum crucible. A tight push-fit lid was then placed on the crucible before placing this in the furnace. The crucible was heated to a temperature up to 1350°C, depending on flux composition and, after allowing 24 hr at the upper temperature, was cooled slowly—usually about 1 deg. C hr^{-1}—to 700°C. The furnace was then turned off, allowing the crucible to cool quickly to room temperature. The flux was then dissolved in dilute nitric acid and the insoluble niobate crystals separated for examination.

Preliminary runs were carried out using mixtures of $(Ba_xSr_{1-x})Nb_2O_6$ with "fluxes" of the formulae $(Ba_xSr_{1-x})B_4O_7$, $(Ba_xSr_{1-x})B_2O_4$ or $(Ba_xSr_{1-x})O \cdot 0.6B_2O_3$; the latter composition is close to a eutectic in both the BaO–B_2O_3 and SrO–B_2O_3 systems (*6*). For all values of x, the tetraborate mixtures gave crystals of chemical composition $(Ba_ySr_{1-y})Nb_2O_6$; the other two fluxes gave crystals of hexagonal $(Ba_zSr_{1-z})_5Nb_4O_{15}$. The ratio of barium:strontium in the crystals (y or z in the above formulae) is dependent on the initial composition in the melt (i.e., x) and also on the proportion of borate flux used. Mixed crystals grown from tetraborate fluxes with $x = 0.5$ give values of $y \sim 0.6$ (see also Table I).

Figure 1 summarizes the observations of the preliminary runs for $x = 1$, that is, for the crystallization of barium niobates from barium borate fluxes. Replacement of barium in the fluxes by strontium, either partially or completely, yielded niobate crystals having the same chemical composition, with the barium partly or totally substituted by strontium.

3. Growth of Ferroelectric Barium–Strontium Niobate

As a consequence of the investigation into barium–strontium borate flux systems, all the later

TABLE I

STRUCTURE AND COMPOSITION DATA FOR BARIUM–STRONTIUM NIOBATE CRYSTALS GROWN FROM BARIUM–STRONTIUM BORATE FLUX

Initial composition of flux mixture (molar ratios) $Ba_xSr_{1-x}Nb_2O_6$: $Ba_xSr_{1-x}B_4O_7$	x	Structure of crystalline product[a]	Average barium content (y) in product, $Ba_ySr_{1-y}Nb_2O_6$
70:30	0.35	T	0.44
	0.50	T	0.58
	0.60	T	0.62
	0.85	T + H	0.88
60:40	0.15	O	0.08
	0.25	O	0.19
	0.40	T	0.46
	0.50	T	0.59
	0.70	T	0.68
50:50	0.35	O	0.46
	0.50	T	0.57
	0.80	T	0.83
	0.90	H	0.96
30:70	0.45	O	0.57
	0.50	T	0.62
	0.60	H	0.72
	0.70	H	0.83
20:80	0.50	O	0.63
	0.60	H	0.73

[a] Structures: T = tetragonal (ferroelectric, BSN), O = orthorhombic (strontium niobate form), H = pseudo-hexagonal (barium niobate form).

crystal growth runs used tetraborate fluxes of composition $Ba_xSr_{1-x}B_4O_7$. Both BaB_4O_7 and SrB_4O_7 have melting points below 1000°C (approximately 910 and 990°C, respectively). More detailed investigation of this flux system revealed that crystals of the tetragonal, ferroelectric, form of $(Ba,Sr)Nb_2O_6$ could be precipitated under restricted conditions, depending on the relative proportions of barium to strontium, and of niobium to boron (i.e., of niobate solute to borate solvent).

At relatively high temperatures, for example from a mixture consisting of 60% $(Ba_xSr_{1-x})Nb_2O_6$ with 40%$(Ba_xSr_{1-x})B_4O_7$ (molar proportions), the tetragonal phase crystallized from compositions having $0.35 \leqslant x \leqslant 0.85$ approximately. Outside this region, the crystalline product was found to have the structure of one of the component niobates, that is $SrNb_2O_6$ (orthorhombic) or $BaNb_2O_6$ (pseudo-hexagonal), depending on the relative proportions of barium and strontium in the melt. The use of a higher proportion of flux, so that crystallization could commence at a lower temperature, indicated a more restricted region of barium:strontium in which the ferroelectric form could be crystallized. If the proportion of flux used was greater than about 70%, then it was not possible to grow material of the tetragonal phase at all, for any proportions of barium to strontium. The products were found to have the structure of either of the component niobates, or to be a mixture of the two. Table I shows the structure and composition of $Ba_ySr_{1-y}Nb_2O_6$ crystals grown from tetraborate fluxes, while Fig. 2 indicates the regions in the $BaNb_2O_6$–$SrNb_2O_6$–BaB_4O_7–SrB_4O_7 system where the three possible crystal forms for the niobate solid solutions are precipitated. Melt growth data (*2*, *4*) suggests that the tetragonal solid solutions can be grown for $0.15 \leqslant x \leqslant 0.80$, approximately. Approximate eutectic compositions were estimated by weighing the products from each run and comparing with the theoretical maximum yield; this composition was found to be in the range 9–14% $(Ba,Sr)Nb_2O_6$ for all proportions of Ba:Sr.

Tetragonal barium–strontium niobate crystals grown from flux at higher temperatures are in the form of pale orange or yellow rods or glassy plates up to 6 mm long by 2 mm cross section (Fig. 3). The crystals from melts with a higher proportion of borate are generally much smaller, probably due to the increased viscosity of the mixture at the lower temperatures at which crystallization commences.

Chemical analysis (*7*) of the growth products confirmed that solid solutions with the $BaNb_2O_6$ or $SrNb_2O_6$ structures were more stable than the tetragonal structure at temperatures well below the melting point. Figure 4 makes use of the analytical results and shows the structure of $(Ba,Sr)Nb_2O_6$ solid solutions crystallizing from a range of flux compositions. The stability of the structures is shown to depend on the barium:strontium proportions in the niobate $(Ba,Sr)Nb_2O_6$ and also on the temperature at which growth commences. However, no direct measurements were made of growth temperatures and these were inferred qualitatively in Fig. 4 by the proportion of flux (in terms of $Ba_xSr_{1-x}B_4O_7$ to $Ba_xSr_{1-x}Nb_2O_6$) at the start of the growth run. Superimposed on this figure is the melting diagram of Carruthers and Grasso (*4*) for the $BaNb_2O_6$–$SrNb_2O_6$ system.

From Fig. 4, it is seen that the composition for maximum stability in the ferroelectric phase appears

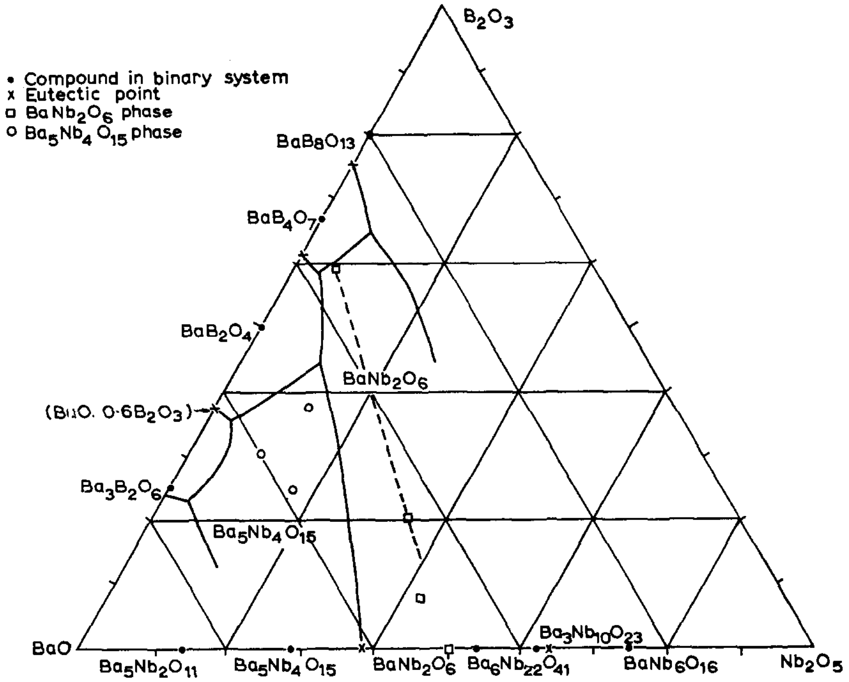

FIG. 1. Partial BaO–Nb_2O_5–B_2O_3 system, showing the approximate stability regions for the crystallization of $BaNb_2O_6$ and $Ba_5Nb_4O_{15}$. The BaO–B_2O_3 and BaO–Nb_2O_5 binary systems are taken from Ref. (*6*). Other information from Ref. (*5*) and from this work. The dashed line indicates the range of compositions found to give crystals of $BaNb_2O_6$ on cooling a melt.

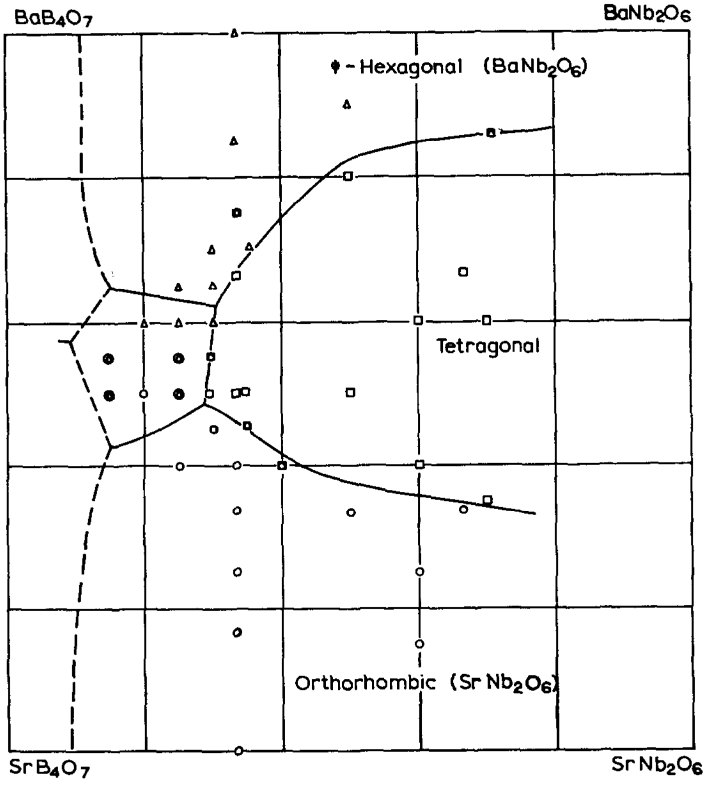

FIG. 2. Crystallization regions in the (Ba,Sr)Nb_2O_6–(Ba,Sr)B_4O_7 system. □ = tetragonal, ○ = orthorhombic, Δ = pseudo-hexagonal solid solutions.

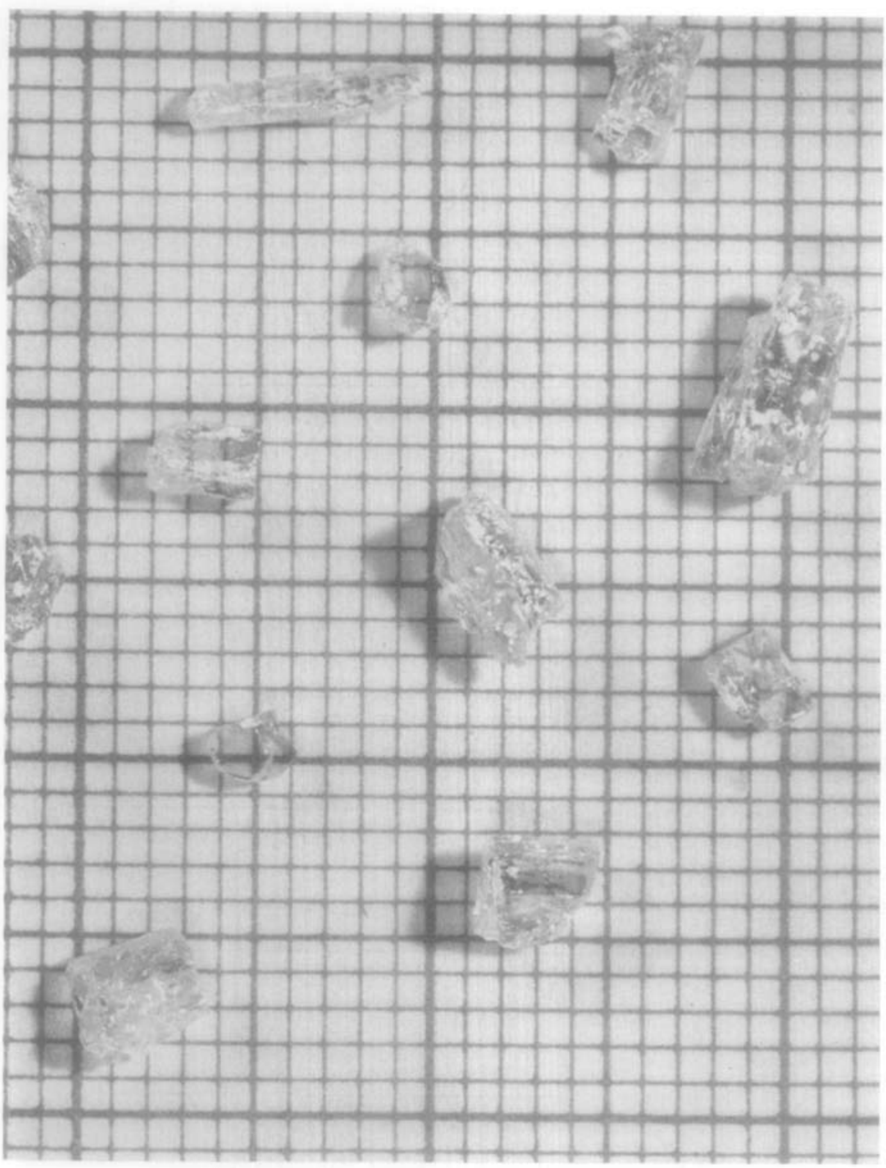

FIG. 3. Flux-grown ferroelectric barium-strontium niobate. (mm grid).

to be in the region of $(Ba_{2/3}Sr_{1/3})Nb_2O_6$. By firing ground flux-grown samples with composition near this value, and with the $SrNb_2O_6$ or $BaNb_2O_6$ structure, it is possible to form the tetragonal phase. It is estimated that the minimum temperature of stability for the tetragonal form is in the region of 850°C. Attempts were made to reconvert tetragonal material to either of the other two forms, by annealing for prolonged periods (up to 7 days) at temperatures below 850°C, but were not successful. Carruthers and Grasso (*4*) have also noted that tetragonal barium strontium niobate was not formed unless their ceramic samples were heated above 1000°C.

4. Conclusions

From the observations made during this study, it is found that crystals of ferroelectric barium strontium niobate can be grown from a BaB_4O_7–SrB_4O_7 flux, but can only be obtained in useful sizes at temperatures approaching the melting point

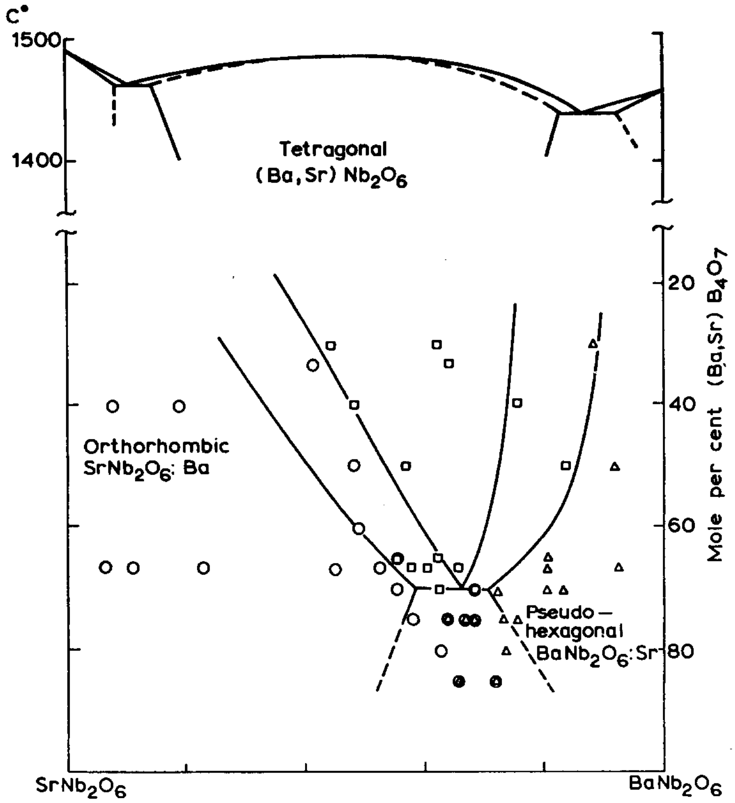

FIG. 4. Stability regions in the $BaNb_2O_6$–$SrNb_2O_6$ system. Symbols are as in Fig. 2. Note change in scale (see text).

of the niobate. It is probable, however, that an improvement in the crystal size would result from controlled seeding of the flux. The results suggest that the tetragonal (ferroelectric) form of $(Ba,Sr)Nb_2O_6$ solid solutions is metastable at temperatures below about 850°C, even for the most stable composition, approximately $(Ba_{2/3}Sr_{1/3})Nb_2O_6$. The stable structures below 850°C are the $SrNb_2O_6$, orthorhombic form (which can contain up to 60 at.% barium substituted for strontium), and the $BaNb_2O_6$, pseudohexagonal form (with up to 30% strontium).

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