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Barium Sodium Niobate: Constitutional Studies and Crystal Growth

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Phase equilibria of barium sodium niobate, stoichiometric formula $Ba_2 NaNb_5O_{15}$ (10 Na_2O, 40 BaO, 50 Nb_2O_5), in the ternary Na_2O-BaO-Nb_2O_5 system have been studied and related to observations made on Czochralski grown single crystals. Extensive solubility occurs in Nb_2O_5-rich specimens, the liquidus and solidus surfaces being extremely flat and close together over the complete homogeneity range. Crystals grown from the non-stoichiometric congruent melting composition (7.2 Na_2O, 42.2 BaO, 50·6 Nb_2O_5) are completely free from growth striae.

1. Introduction

The useful non-linear optical properties of barium sodium niobate* have led to considerable interest in the growth and assessment of B-S-N single crystals [1].

Many of the early problems associated with the Czochralski growth of crack-free single crystals and the suppression of microtwinning have now been solved in B-S-N [1, 2]. However, a further problem arises from the presence of growth striae which cause undesirable changes in refractive index and impair device performance. The occurrence of such striae has been attributed to localised variations in the composition of the material in response to temperature fluctuations. Hitherto, efforts to remove striae have concentrated upon the reduction of temperature fluctuations by growth under low temperature gradient conditions [3, 4]. Controlled growth is difficult under these conditions, and an alternative approach is to grow crystals at the composition where the solidus and liquidus are coincident, i.e. the congruent melting composition. Growth striae should not be present in such crystals because temperature fluctuations cannot alter the solidifying composition. In order to locate this composition it is desirable to have an accurate knowledge of the homogeneity range and the shape of the liquidus and solidus surfaces within this range. It is the purpose of the present paper to report related studies of the ternary phase equilibria and crystal growth of B-S-N. During the course of this work, similar constitutional investigations have been reported [5-7]. Whilst some of the present results are in agreement with those published, there are important discrepancies which are discussed in section 4.

2. Experimental Techniques

Constitution studies were made on both B-S-N melts and Czochralski-grown single crystals.

Melt compositions were prepared from carefully dried $NaNO_3$, $Ba(NO_3)_2$ and Nb_2O_5 powders supplied by Johnson-Matthey Co. After maintaining the molten mixture in platinum crucibles for 2 h, in order to allow for the complete decomposition of the nitrates, the samples were rapidly solidified on a cold platinum sheet.

B-S-N single crystals were prepared from the melts using a modified Czochralski technique. The crystals were pulled from platinum crucibles in a 100% O_2 atmosphere at respective pull and rotation rates of 8 mm h^{-1} and 20 rpm.

Independent analyses of the melts and crystals in terms of Nb_2O_5, BaO and Na_2O content were performed by AERE (Harwell) and the Plessey Co. (Caswell). The following limits of accuracy were reported for the compositions of all specimens: Nb_2O_5 ± 0.5 mole %, BaO ±

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* Hereafter referred to as B-S-N

0.3 mole %, Na_2O ± 0.1 mole %.

The constitution of B–S–N melts and crystals was investigated by DTA and X-ray diffraction techniques. A Netsch, 1550 DTA apparatus, incorporating Pt/Pt-Rh thermocouples and platinum crucibles, was used to determine solidus and liquidus temperatures (± 2° C) during heating. Linear heating rates of either 1 or 2° C min^{-1} did not result in superheating, whereas considerable undercooling of up to 100° C was observed when the B–S–N liquids were cooled at 1 or 2° C min^{-1}. Consequently, measurements were always made on the heating curves.

Room temperature phase equilibria data of B–S–N were obtained from Debye-Scherrer X-ray powder patterns using CrKα radiation. The *d*-spacings of all reflections with Bragg angles in the ranges 0 to 45 and ~ 50 to ~ 80° were measured to within ± 0.001 Å and ± 0.0001 Å respectively.

3. Results

3.1. Room Temperature X-ray Diffraction Observations

The data on the room temperature homogeneity range of B–S–N are presented in fig. 1 for which an asterisk denotes the stoichiometric composition, $Ba_2NaNb_5O_{15}$, and a dotted line the B–S–N homogeneity range. Single-phase specimens, based on the orthorhombic crystal structure, are indicated in fig. 1 by open circles; all other specimens contained two or three phases as shown in the key. The σ-phase corresponds to that reported by Carruthers and Grasso [7]. Good agreement between the two investigations was obtained for the *d*-spacings of the σ-phase (table I).

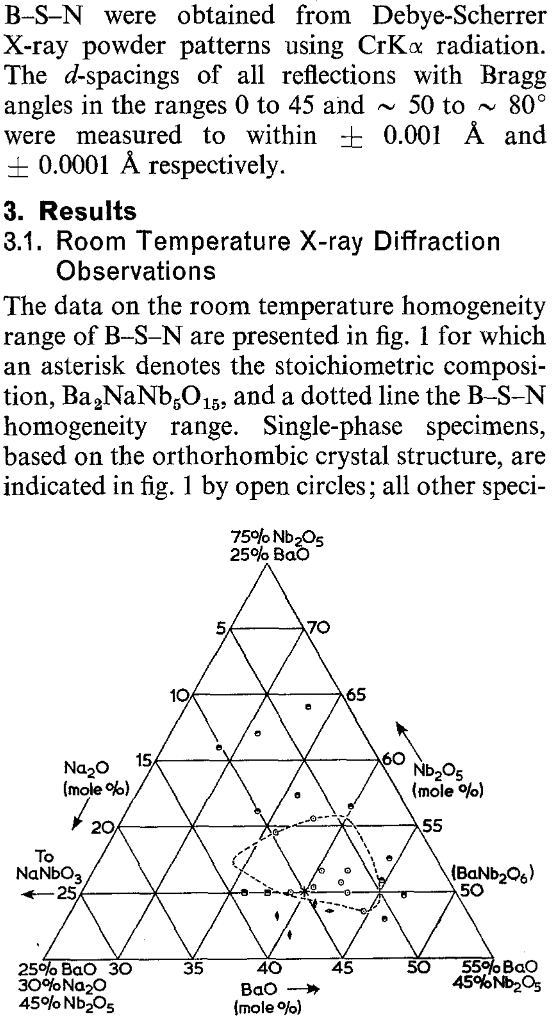

Figure 1 The room temperature homogeneity range of barium sodium niobate. *, stoichiometric composition $Ba_2NaNb_5O_{15}$; – – –, barium sodium niobate phase boundary; ○, single-phase orthorhombic B–S–N; ◓, B–S–N + $BaNb_2O_6$; ▣, B–S–N + $NaNbO_3$; ◈, B–S–N + σ; ◆, B–S–N– + $NaNbO_3$ + σ.

TABLE I The *d*-spacings of the σ-phase in the Nb_2O_5–BaO–Na_2O system, as determined in the present investigation and by Carruthers and Grasso [7].

Present investigation *d* (Å)	Carruthers and Grasso [7] *d* (Å)
2.885	2.90
2.042	2.05
1.668*	1.67
1.454*	1.445
1.294*	1.292

* Broad diffraction lines, due to presence of B–S–N reflections.

The homogeneity range of B–S–N along the binary $NaNbO_3$–$BaNb_2O_6$ join extends from 11.6 Na_2O, 38.4 BaO, 50 Nb_2O_5 to 5.0 Na_2O, 45.0 BaO, 50 Nb_2O_5. Melts deficient in Nb_2O_5 showed very limited solubility. However, melts containing an excess of Nb_2O_5 showed extensive solubility and, on the basis of the DTA results (section 3.2), the B–S–N phase boundary is drawn through the compositions 9.6 Na_2O, 35.8 BaO, 54.6 Nb_2O_5 and 6.6 Na_2O, 37.9 BaO, 55.5 Nb_2O_5, as shown in fig. 1.

Numerous B–S–N crystals have been grown within the single-phase region. The X-ray diffraction data of these crystals and the rapidly solidified compositions showed that the *c*-spacing of the orthorhombic unit cell decreases significantly with an increase in Nb_2O_5 content (table II).

3.2. DTA Measurements

Liquidus and solidus isotherms of B–S–N specimens are plotted in figs. 2 and 3 respectively; the relevant data for the binary Nb_2O_5–BaO system [8] are also included in fig. 2. The liquidus temperatures of the single-phase B–S–N specimens were within the range 1430 to 1455° C which shows that the liquidus surface is extremely flat over the complete composition range. A phase transformation at 1320° C was observed on heating the eight Nb_2O_5-rich melts, including the 9.6 Na_2O, 35.8 BaO, 54.6 Nb_2O_5 and 6.6 Na_2O, 37.9 BaO, 55.5 Nb_2O_5 specimens

TABLE II The decrease in the *c*-spacing with an increase in Nb_2O_5-content of B–S–N, measured from (002)reflections

Specimen composition Na_2O (± 0.1 mole %)	BaO (± 0.3 mole %)	Nb_2O_5 (± 0.5 mole %)	*c*-spacing (± 0.001 Å)
6.8	44.6	48.6	4.000
7.2	42.8	50.0	3.996
7.2	42.1	50.7	3.995
7.2	41.6	51.2	3.994
7.3	41.1	51.6	3.993
6.6	37.9	55.5	3.976
6.8*	35.9	57.3	3.972
7.1*	30.9	62.0	3.977

* The diffraction patterns of these specimens exhibited weak lines in addition to those characteristic of the B–S–N phase.

which revealed single-phase B–S–N powder patterns at room temperature. On cooling these Nb_2O_5-rich melts, the 1320° C transformation was evident, together with an additional transformation at 1290° C.

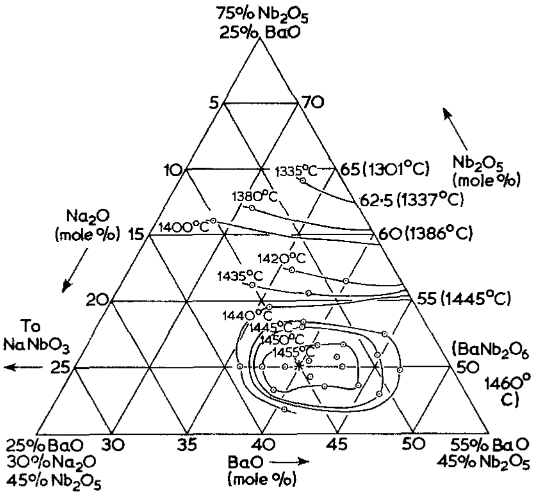

Figure 2 Liquidus isotherms of barium sodium niobate. *, stoichiometric composition $Ba_2NaNb_5O_{15}$.

The small homogeneity range of B–S–N at compositions deficient in Nb_2O_5 was manifested by a steeply inclined solidus surface (fig. 3). The DTA peaks corresponding to liquidus and solidus temperatures were extremely close together over the range of Nb_2O_5-rich B–S–N specimens and, for these compositions within the 1455° C liquidus isotherm, it became impossible to resolve the individual peaks. Measurements of the DTA peak widths showed that the composition range enveloped by the 1455° C solidus isotherm (area A in fig. 3), was considerably smaller than that enveloped by the 1455° C liquidus isotherm (figs. 2 and 3). These observations show, therefore, that the congruent melting composition does not coincide with the stoichiometric composition, but lies within area A of fig. 3.

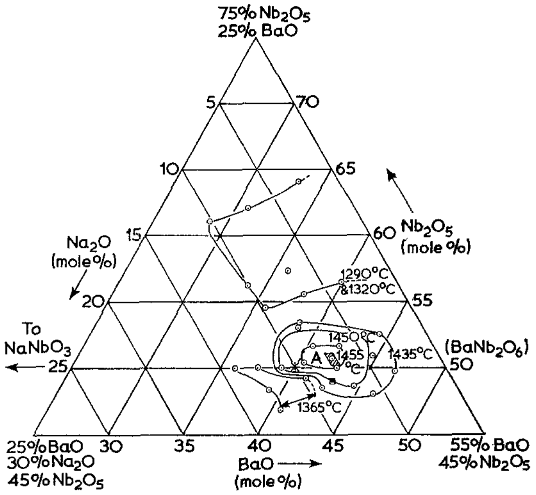

Figure 3 Solidus isotherms of barium sodium niobate. *, stoichiometric composition $Ba_2NaNb_5O_{15}$; ▨, area containing congruent melting composition of B–S–N from present investigation; ■, congruent melting composition of B–S–N proposed by Carruthers and Grasso [7].

3.3. Crystal Growth Observations

Analyses of crystals grown from melts prepared from previously pulled crystals showed that the final composition invariably lay within the region A in fig. 3. Such crystals still contained growth striae. If, however, the original melt composition was within area A (fig. 3), the re-pulled crystals were found to be striae-free. Analyses of these crystals indicated a composition of 7.2 Na_2O, 42.2 BaO, 50.6 Nb_2O_5. The error-range associated with these analyses delineates the shaded area of the phase field (fig. 3) within which the congruent melting composition must lie. The congruent melting composition, proposed by Carruthers and Grasso [7] (8 Na_2O, 43 BaO, 49 Nb_2O_5), is included in fig. 3 for comparison with the present observations.

4. Discussion

The room temperature homogeneity range of B–S–N along the binary $NaNbO_3$–$Ba_2Nb_2O_6$ join and over compositions deficient in Nb_2O_5 (fig. 1), is in good agreement with reported data [5-7]. The small homogeneity range of B–S–N in Nb_2O_5-deficient specimens reflects the stability of the NbO_6 octahedra and the difficulty in creating niobium vacancies in the B–S–N lattice. On the other hand, excess niobium ions can readily be accommodated in the B–S–N lattice by contracting the *c*-spacing of the orthorhombic cell. This is also in general agreement with previous observations [6, 7], although the extent of the B–S–N phase field for Nb_2O_5-rich compositions (fig. 1) is not as large as that reported by Giess *et al* [6] and Carruthers and Grasso [7]. The room temperature phase boundary in fig. 1 terminates at the compositions 9.6 Na_2O, 35.8 BaO, 54.6 Nb_2O_5 and 6.6 Na_2O, 37.9 BaO, 55.5 Nb_2O_5 since these specimens, although apparently single-phase from the X-ray powder patterns, exhibited the 1290 and 1320° C transformations. The latter temperatures are in good agreement with those reported for the reaction $(BaO)_6 . (Nb_2O_5)_7 + (BaO)_3 . (Nb_2O_5)_5 \rightarrow (BaO)_6 . (Nb_2O_5)_7$ + liquid and $(BaO)_6 . (Nb_2O_5)_7$ + liquid $\rightarrow$ (BaO) . (Nb_2O_5) + liquid in the binary Nb_2O_5–BaO system [8]. However, in the present investigation the X-ray reflections from the second phase in the Nb_2O_5-rich specimens corresponded to those from $BaNb_2O_6$. These observations differ from those of Carruthers and Grasso [7] who reported only a single reaction at 1290° C for Nb_2O_5-rich specimens containing B–S–N + $(BaO)_3 (Nb_2O_5)_5$.

Observations on the crystal growth of B–S–N (section 3.3) indicate that the congruent melting composition is on the Nb_2O_5-rich side of the stoichiometric composition rather than the Nb_2O_5-deficient side, as proposed by Carruthers and Grasso [7]. The congruent melting composition, proposed by Carruthers and Grasso [7], coincides with the phase boundary of the present investigation, and in fact significant amounts of second phase were observed in melts of this composition. Carruthers and Grasso [7] report the growth of crystals with the congruent melting composition from stoichiometric melts whereas all stoichiometric melts in the present investigation yielded crystals deficient in Na_2O and containing an excess of Nb_2O_5 (i.e. in the area A of fig. 4). The reasons for these discrepancies are not fully understood, although they may be associated with the differences in the methods and limits of accuracy of determining specimen compositions. In the present investigation all B–S–N melts and crystals were analysed to within the limits given in section 2, whereas the limits of accuracy of Carruthers and Grasso's [7] data, were not reported.

5. Conclusions

(i) A determination of the ternary phase field of barium sodium niobate in the Na_2O–BaO–Nb_2O_5 system has shown that extensive solubility occurs in specimens deficient in Na_2O and rich in Nb_2O_5, whereas specimens deficient in Nb_2O_5 show very limited solubility.

(ii) The liquidus and solidus surfaces over the barium sodium niobate phase field are extremely flat.

(iii) The congruent melting composition (7.2 Na_2O, 42.2 BaO, 50.6 Nb_2O_5) does not coincide with the stoichiometric composition (10 Na_2O, 40 BaO, 50 Nb_2O_5).

(iv) Barium sodium niobate crystals which are grown from the congruent melting composition are striae-free.

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