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Phase studies of the system Li_2O–BaO–Nb_2O_5 in relation to Czochralski growth problems of $Ba_2LiNb_5O_{15}$ single crystals

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$Ba_2LiNb_5O_{15}$ (BLN) is an interesting alternative material to the well known $Ba_2NaNb_5O_{15}$ (BSN) for frequency doubling of 1.06 μm YAG laser radiation. Contrary to BSN, no exact details of the BLN phase diagram system were available. Therefore, Czochralski growth of single crystals with an homogeneity range, being desirable for practical applications, appeared difficult. To obtain these important data, appropriate studies of the ternary system BaO–Li_2O–Nb_2O_5 were made. For this the binary sections Li_3NbO_4–$BaNb_2O_6$ and $LiNbO_3$–$BaNb_2O_6$ were selected along with further compositions near the stoichiometric ratio and investigated by means of differential thermal analysis and X-ray phase analysis techniques. The results of these investigations, and their application to crystal growth, were tested by selected growth experiments.

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1. Introduction

$Ba_2LiNb_5O_{15}$ (BLN) crystallizing in the tetragonal-tungsten-bronze structure, possesses favourable properties for frequency doubling of 1.06 μm YAG laser radiation [1, 2]. The experimental data for the growth of crack-free single crystals of this niobate using the Czochralski technique are reported in [3], the investigation of the macrostructure in the crystals in [4]. However, the initial melt compositions used for crystal growth were in the region of the stoichiometric ratio and produced crystals of a non-optimal homogeneity for the desired application. These results suggested the use of other starting compositions of the ternary system BaO–Li_2O–Nb_2O_5 which give more favourable supposition of the crystal growth. So far phase diagram investigations have been made in binary edge systems BaO–Nb_2O_5 [5] and Li_2O–Nb_2O_5 [6] and some measurements of the liquidus temperature have been obtained in the system $LiNbO_3$–$BaNb_2O_6$ [7]. Detailed knowledge of the constitutional conditions in the ternary-phase field, especially in the region of the composition BLN, were not available. To overcome the phase separation problem [4], it was necessary to determine additional data in the phase diagram of the ternary system BaO–Li_2O–Nb_2O_5. These data were obtained by analysing the sections between the compositions lithium-metaniobate-bariumniobate ($LiNbO_3$–$BaNb_2O_6$) and lithium-orthoniobate-bariumniobate (Li_3NbO_4–$BaNb_2O_6$)* of the binary edge systems Li_2O–Nb_2O_5 and BaO–Nb_2O_5 and compositions with more than 50 mol% Nb_2O_5.

2. Experimental

The phase diagram investigation was carried out by means of differential thermal analysis (DTA) and X-ray phase analysis. The DTA-experiments were made using a Netzsch-apparatus with a maximum operating temperature of 1550°C. Various mixtures (300 to 500 mg) of powdered $LiNbO_3$, Nb_2O_5†, $BaCO_3$ and Li_2CO_3‡ were filled into platinum DTA crucibles (6 mm diameter, 12 mm length) and, for consistency in measurement, heated several times up to 1500°C

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*Hereafter denoted as $LiNbO_3$ = LN, Li_3NbO_4 = L_3N, $BaNb_2O_6$ = BN.
†Supplied as grade I with maximum impurities 100 ppm, from MERCK, Darmstadt.
‡Supplied as grade I with maximum impurities 100 ppm, from STARCK, Goslar.

with heating rates ranging between 2 and 10°C min^{-1}.

The products were then powdered and the phases present identified by X-ray analysis using a Philips-powder-diffractometer. From the thermal effects of the DTA curves and the results of the phase analyses, the phase diagram for the ternary system $BaO–Li_2O–Nb_2O_5$ was constructed according to Gäumann [8] and Etter *et al.* [9]. The limits of error lay between $\pm$ 5°C in temperature and $\pm$ 1 mol % in composition.

With selected compositions from the constructed diagram, crystal growth experiments using the Czochralski-technique were carried out under growth conditions as described in [3].

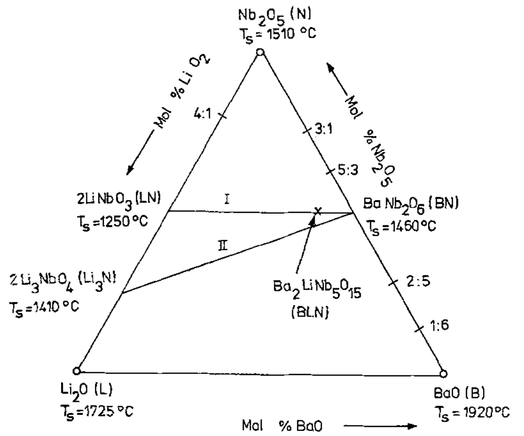

Figure 1 The system $Li_2O–BaO–Nb_2O_5$ with ternary compounds and selected binary sections.

3. Results

A survey of the phase field of the system $BaO–Li_2O–Nb_2O_5$ is shown in Fig. 1. The positions of the composition BLN (corresponding to 40 mol % BaO, 50 mol % Nb_2O_5 and 10 mol % Li_2O) and of the compounds which have already been determined in the edge systems $BaO–Nb_2O_5$ and $Li_2O–Nb_2O_5$ are marked. Also shown are the binary sections selected for this investigation between the compounds 2 LN–BN (I) and 2 L_3N–BN (II). The DTA and X-ray results are shown in Figs. 2 and 3 in the form of phase diagrams for the above-mentioned sections for temperatures above 1100°C. Possible changes below this temperature were not investigated here in detail. The liquidus temperatures in sections I and II can be considered as correct. The solidus regions of the BN-rich sides are not absolutely certain because of the appearance of a peritectic compound as perhaps no equilibrium conditions could be reached using DTA.

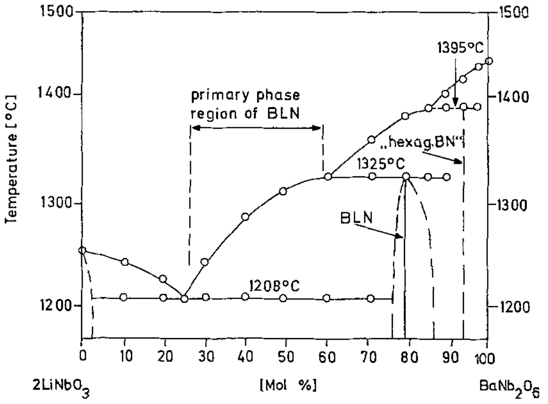

Figure 2 Binary section 2 $LiNbO_3–BaNb_2O_6$ of the ternary system $Li_2O–BaO–Nb_2O_5$.

In section I (see Fig. 2) the phases LN and BLN were present up to 62 mol % BN. Above 62 mol % BN, in addition to these two phases, an increasing proportion of hexagonal BN was present. At 80 mol % BN, a BLN phase, melting incongruently at 1325°C was observed and at approximately 95 mol % BN, a second compound with an hexagonal symmetry also melting incongruently at 1395°C was found. Up to 50 mol % BN, these observations coincide with those of Giess *et al.* [7]. However, beyond this region the liquidus and the reaction temperatures of the peritectic did not agree. For example, in [7] the peritectic is located at 55 mol % BN and 1345°C. The thermal effects above 85 mol % BN which were explained as peritectic reaction were not observed in [7]. In section I (Fig. 2) the

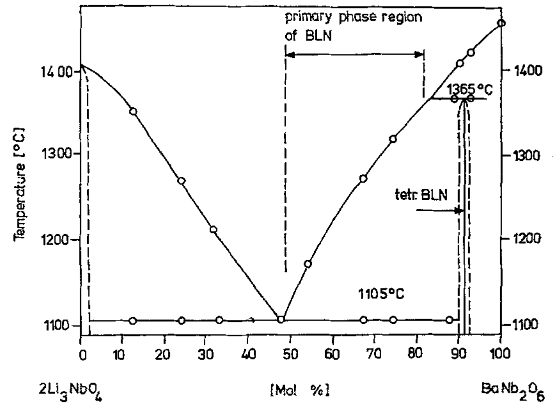

Figure 3 Binary section 2 $Li_3NbO_4–BaNb_2O_6$ of the ternary system $Li_2O–BaO–Nb_2O_5$.

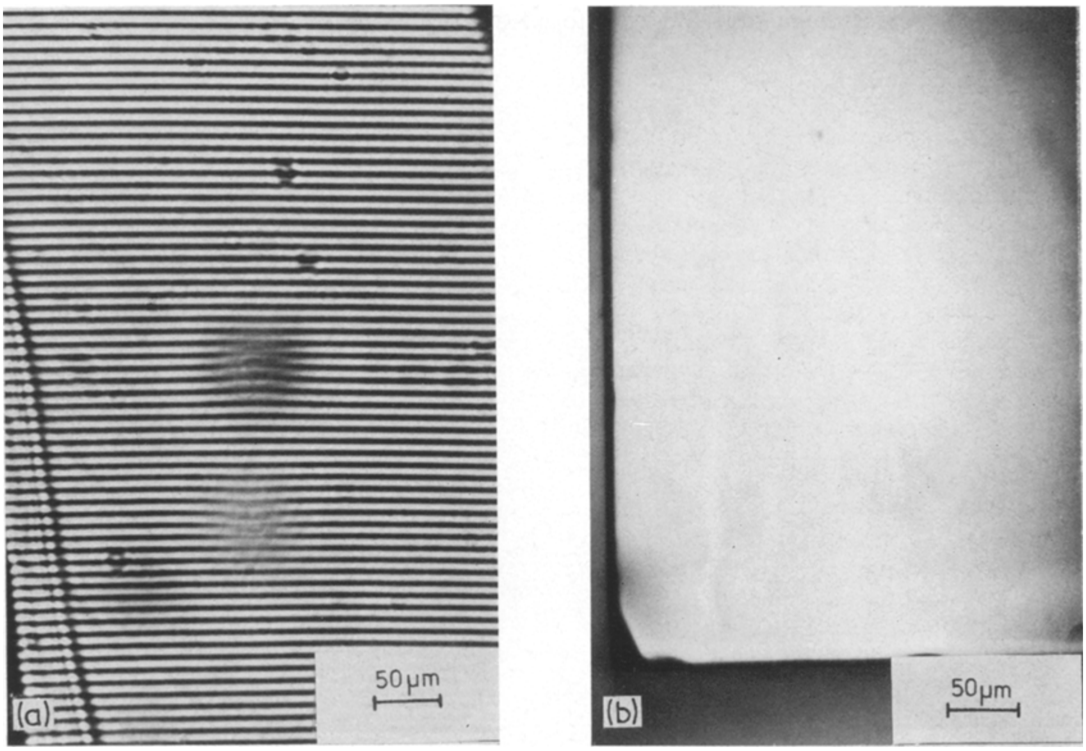

Figure 4 Unetched BLN samples in transmitted light. (a) Striated sample grown from melt with nearly stoichiometric ratio. (b) Striation-free sample grown from melt with 80 mol % BN (section II).

BLN phase shows a distinct existence above 1200°C between 77 and 87 mol % BN.

In section II (Fig. 3) there exists a eutectic with 47.5 mol % BN at 1105°C and a peritectic with 84 mol % BN and at 1365°C. A barium-lithium-niobate phase with tetragonal-tungsten-bronze structure was identified between 90 and 92.5 mol % BN. Its lattice constants at room temperature were determined to be $a = 12.509(9)$ Å, $c = 3.998(4)$ Å.

4. Discussion

The phase diagrams shown in Figs. 2 and 3 help to explain the problems and observations encountered in earlier crystal growth attempts and give important hints for better growth conditions. It follows from Fig. 2 that primary crystallization of the barium-lithium-niobate phase with the tetragonal-tungsten-bronze structure is not possible from stoichiometric melts. Contrary to this, however, single crystals could be obtained from melts, originally weighed out to stoichiometric quantities, after first pulling several polycrystalline boules. The reason proposed is that these boules were of varying compositions thus producing concentration changes in the residual melt until a composition favourable for single crystal growth was reached. It must also be assumed that the melt composition changes due to component evaporation, since a sublimate was observed on the growth chamber wall. It can be seen in Fig. 2 that the primary phase field for the barium-lithium-niobate phase with tungsten-bronze structure lays between 30 and 60 mol % BN. From the slope of the solidus line a distinct influence of the temperature oscillations on the homogeneity of the crystals can be derived. Such periodic oscillations in the crystal compositions have actually been observed and reported [4].

A hint for the growth of homogeneous crystals can be obtained from the phase diagram of section II (Fig. 3). The crystallization of the tungsten-bronze phase is possible with melt compositions between 50 and 80 mol % BN. As the width of the existence range of the tungsten-bronze phase is smaller than in section I it is to be expected that in this region the conditions for crystal growth are more favourable. Since due to the steep fall off of the phase boundary the inevitable temperature oscillations during the crystal growth can only then be an insignificant cause of compositional changes in the crystalline phase. Contrary to earlier work [4], constitutional supercooling should not be so prolific since the difference in the composition of the liquid to solid phase is small. This consideration was confirmed by crystal growth using melt compositions of section II. With 80 mol% BN, no compositional fluctuations in the crystal were observed (Fig. 4). Unfortunately, evaporation losses must have also occurred here since these favourable growth conditions were difficult to maintain over a longer period of time.

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