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Journal of Alloys and Compounds 386 (2005) 246–252

Journal of ALLOYS AND COMPOUNDS

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Ternary system Li_2O–K_2O–Nb_2O_5 Part II: Growth of stoichiometric lithium niobate

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Received 26 December 2003; accepted 30 April 2004

Abstract

Growth conditions of stoichiometric or near-stoichiometric lithium niobate (sLN) from K_2O containing fluxes have been studied by investigating phase equilibria in the ternary system Li_2O–K_2O–Nb_2O_5. The crystallization area of $LiNbO_3$ was confirmed by growth experiments on the g1 ($LiNbO_3$–K_2O), g2 ($LiNbO_3$–ternary eutectic liquid (E_t: 45.0 ± 1.5 mol% Nb_2O_5, 26.0 ± 1.5 mol% K_2O and 29.0 ± 1.5 mol% Li_2O)) and g3 ($LiNbO_3$–$KNbO_3$) joins. The yield and the composition of $LiNbO_3$ single crystals were tested for a wide range of starting compositions. From these experiments, the starting compositions leading to stoichiometric lithium niobate have been determined.

Keywords: Crystal growth; X-ray diffraction; Nonlinear optics; Thermal analysis

1. Introduction

In the binary system Li_2O–Nb_2O_5 [1–4], lithium niobate $LiNbO_3$ (LN) melts congruently with the composition of about 48.6 mol% Li_2O and single crystals can be grown from melt by the Czochralski technique. The lithium deficiency in the congruent crystals leads to intrinsic structural defects and affects many physical properties. Therefore, there exists a significant demand for stoichiometric or quasi-stoichiometric crystals having a perfect crystal lattice and improved properties.

One of the most effective methods of growing stoichiometric $LiNbO_3$ (sLN) single crystals is the high temperature top-seeded solution growth (HTSSG) technique from K_2O–Li_2O–Nb_2O_5 fluxes [5]. In this method, the growth usually starts from a composition with Li/Nb ratio either 1 or 0.945 (ratio of the congruently melting lithium niobate) and K_2O added from 10 to 16 mol%. Recently, we have shown that the real composition of the HTSSG grown crystals depends to a large extent on the choice of the appropriate crystallization temperature and, therefore, of the starting melt composition [6]. Thus, the optimization of the flux and growth conditions requires an extended knowledge of the crystallization range of $LiNbO_3$ in the Li_2O–K_2O–Nb_2O_5 system.

In previous works [7–8], we reported phase equilibrium studies on the ternary system Li_2O–K_2O–Nb_2O_5. Part I [8] of this work presents in detail the solid–liquid equilibria near the $LiNbO_3$ compound. In this report, based on the results of these studies, some issues of the stoichiometric LN single crystal formation are treated:

- Determination of the limits of $LiNbO_3$ liquidus surface and investigation of the yield of $LiNbO_3$ single crystal depending on the starting composition.
- Outline of the area where stoichiometric or near-stoichiometric single crystalline $LiNbO_3$ can be grown.

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2004.04.151

2. Experimental methods

Crystals were grown by the HTTSSG method in a diameter controlled growth apparatus. The technical details of the material synthesis and crystal growth are given in refs. [5,7]. The starting materials used were Starck LN grade Nb_2O_5 and Merck Suprapure K_2CO_3 and Li_2CO_3 pre-reacted in the solid phase. Generally the maximum amount of the $LiNbO_3$ single crystal phase was pulled out, after which the growth process was continued and then, "new" phases were crystallized. Thus, from the yield of $LiNbO_3$, the mass balance of the crystallization can be obtained and the co-ordinates of the limits of $LiNbO_3$ liquidus surface can be calculated and compared with those given by the phase diagram.

The constituent phases were assessed by X-ray powder diffraction analysis with a Philips PW 1710 diffractometer using Cu Kα radiation in the 2θ range of 0–80°. The overall composition of the new phases and remaining flux were determined by chemical analysis of the major components. In these experiments, the $LiNbO_3$ crystals were pulled in 18 mm diameter along the $\langle 00.1\rangle = Z$-axis with a rate of 0.1–0.2 mm/h and rotation speed of 6–28 rpm. The real stoichiometry of the crystals and its evolution during the growth were determined by using a standardized spectroscopic test recording the UV absorption edge position of slices cut along the growth axis from the top to bottom part of the crystal [9].

3. Results and discussion

In the ternary system, all compositions are expressed as molar percentages of Nb_2O_5 (X) and K_2O (Y).

3.1. Assessment of the phase diagram by crystal growth experiments

The polythermal projection of $LiNbO_3$ crystallization field in the ternary system Li_2O–K_2O–Nb_2O_5 is shown in Fig. 1 as presented in Part I [8]. Accordingly, the $LiNbO_3$ liquidus surface is well determined above the $LiNbO_3$–$KNbO_3$ join, but beyond it and for Nb_2O_5 contents higher than 50–55mol%, the outlined equilibrium domains are only estimated. Thus, the $LiNbO_3$ liquidus surface is limited by four monovariant lines: Liq + Li_3NbO_4 + $LiNbO_3$, Liq + $KNbO_3$ + $LiNbO_3$, Liq + "KLN solid solution" + $LiNbO_3$ and Liq + $LiNb_3O_8$ + $LiNbO_3$ (the term "KLN solid solution" is used for the ternary tungsten bronze-type solid solution encountered beyond Nb_2O_5 = 50 mol% and K_2O = 25 mol%). At 997 °C, the ternary eutectic reaction occurs between liquid, $LiNbO_3$, β-Li_3NbO_4 and $KNbO_3$. The composition of the eutectic liquid (E_t) is 45.0 ± 1.5 mol% Nb_2O_5, 26.0 ± 1.5 mol% K_2O and 29.0 ± 1.5 mol% Li_2O. A quasi-peritectic reaction has also been identified at a temperature of about 1050–1055 °C. The quasi-peritectic liquid (T) has a composition roughly equal to: 49 mol% Nb_2O_5, 25.5 mol% K_2O and 25.5 mol% Li_2O.

Up to now, the single-crystal growth technique of sLN was experienced only along the $LiNbO_3$–K_2O (Y = 100–2X) join: i.e. from fluxes with starting composition of a [Li]/[Nb] ratio equal/or near to 1 and with various potassium oxide contents [5–10]. In the present work, growth experiments have been conducted from various fluxes listed in Table 1. This table summarizes growth results and the constituent phases identified in the grown boules as well. In these growth experiments, besides the starting compositions located on the $LiNbO_3$–K_2O line (labelled as g1 in Table 1 and in Fig. 1),

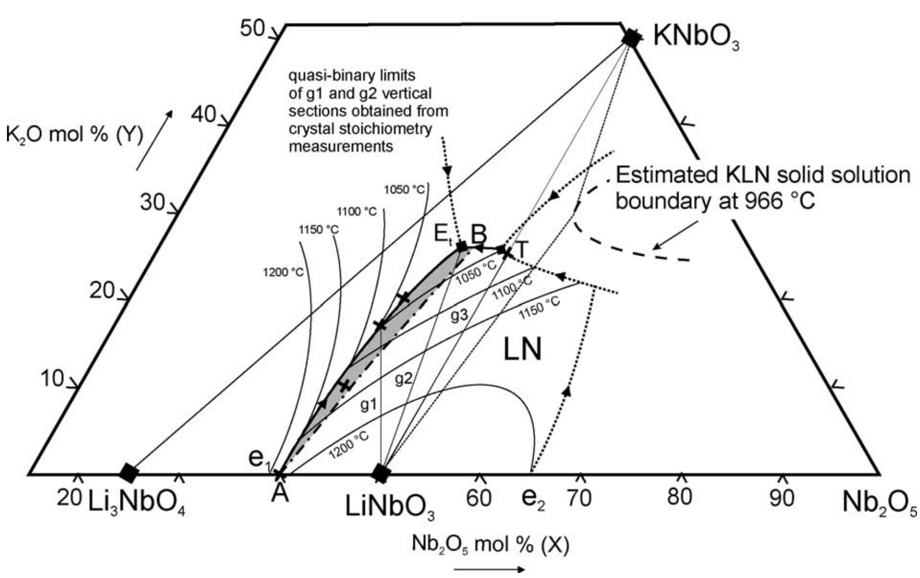

Fig. 1. Expanded view of the polythermal projection of $LiNbO_3$ crystallization field (E_t: $LiNbO_3$–Li_3NbO_4–$KNbO_3$ ternary eutectic point, T: ternary quasi-peritectic point, e_1: $LiNbO_3$–Li_3NbO_4 binary eutectic point, e_2: $LiNbO_3$–$LiNb_3O_8$ binary eutectic point), light grey area: crystallization region of fully stoichiometric lithium niobate (LN), line AB: quasi-binary limit (see text).