INVESTIGATION OF NEW FLUXES FOR THE SINGLE-CRYSTAL GROWTH OF STOICHIOMETRIC LITHIUM NIOBATE
Phase relations in the ternary system Cs_2O–Li_2O–Nb_2O_5

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Thermoanalytical and crystal growth investigations of the ternary system Cs_2O–Li_2O–Nb_2O_5 are presented in order to grow stoichiometric $LiNbO_3$ (LN) crystals. Part of the phase diagram is determined and subsolidus phases are identified at room temperature by X-ray powder diffraction. Among the constituent phases, a new tetragonal cesium lithium niobate phase is assessed. From the Cs_2O–Li_2O–Nb_2O_5 system, good quality quasi-stoichiometric LN crystals can be grown.

Keywords: crystal growth, flux, phase diagram, stoichiometric lithium niobate

Introduction

The lithium niobate (LN) crystal is a ferroelectric material with excellent non-linear properties. It is applied in electro-optics, laser physics, holography, frequency conversion of laser diodes and modulators. While the stoichiometric LN (sLN, [Li]/[Nb]~1) crystal has excellent properties and is preferred in many cases, the congruent LN (cLN, [Li]/[Nb]~0.945) crystal has high Li-deficiency which limits its technical applications. Several methods exist for growing sLN single crystals [1, 2], one of them is the high temperature top seeded solution growth (HTTSSG) [1]. An ideal flux significantly lowers the crystallization temperature determining the stoichiometry of the crystal and the extra does not enter the lattice allowing the growth of defect free crystals. For growing sLN, the K_2O–Li_2O–Nb_2O_5 ternary mixture was used so far [3, 4] but with limited yield (20 mass%). Solvents, based on other alkali metal oxides (Na_2O, Cs_2O and Rb_2O) can be candidates for the growth of sLN crystals too [5], may be with a higher crystallization yield.

Experimental

The raw materials used were Cs_2CO_3 (Merck, Extra pure), Li_2CO_3 (Merck, Suprapur) and Nb_2O_5 (Starck, LN grade). The Cs_2O–Li_2O–Nb_2O_5 samples were dried, mixed and reacted in solid phase (800°C for 12 h), then after a second mixing, they were treated again at 800°C for 12 h and finally ground.

Four isopleths were selected for investigation: the first corresponds to the equation: [Cs_2O mol%]=100-2[Nb_2O_5 mol%] with 5–25 mol% in Cs_2O, the second isopleth is [Nb_2O_5 mol%]=50 and the last two correspond to [Cs_2O mol%]=10 and 20 with 35<[Nb_2O_5 mol%]<55 (Fig. 1).

The crystallization and phase transition temperatures of Cs_2O–Li_2O–Nb_2O_5 ceramic samples were determined with a Mettler-Toledo TGA/SDTA 851e apparatus with a heating rate of 10°C min^{-1}. The constituent phases were assessed by X-ray powder diffraction with an INEL MPD CPS 120 diffractometer using CuK_α radiation.

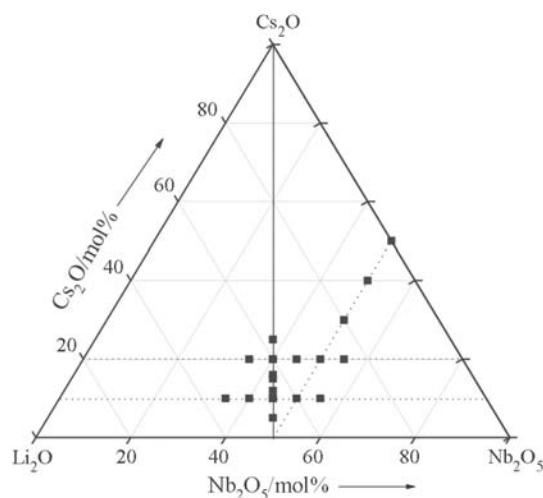$LiNbO_3$ crystals were grown by the HTTSSG method from fluxes containing 10 mol% Cs_2O and

Fig. 1 Composition of ceramic samples investigated by thermal analysis and X-ray diffraction

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having [Li]/[Nb]=1 starting composition. For the growth of large single crystals <00.1> seed orientation was applied. The crystals were pulled at rates of 0.3–0.5 mm h^{-1} and rotated with 8–10 rpm. The crystal growth method is detailed in [5].

The cesium content of the crystals was analyzed by the atomic absorption spectroscopic (AAS) method. The samples were digested with a mixture of HF and HNO$_3$ acids. For the characterization of the crystal composition the UV absorption edge was measured using a Jasco V-550 UV/VIS spectrophotometer with a wavelength accuracy of 0.3 nm.

Results and discussion

X-ray diffraction analyses allowed determining sub-solidus equilibria in the investigated part of the diagram (Fig. 2). At room temperature, we identified:

- a single-phase domain of an unknown ternary solid solution called '*X*' which exists in the same composition range as the tetragonal tungsten bronze type '$K_3Li_2Nb_5O_{15}$' solid solution (KLN) in the K_2O–Li_2O–Nb_2O_5 system.
- two two-phase domains: *X*+β-Li$_3$NbO$_4$ (L3N) and *X*+LiNbO$_3$ (LN)
- two three-phase regions: CsNbO$_3$ (CN)+*X*+β-Li$_3$NbO$_4$ and *X*+LiNbO$_3$+β-Li$_3$NbO$_4$.

The X-ray diffraction pattern of *X* is given in Table 1. It could be indexed in a tetragonal structure with: *a*=10.986 Å and *c*=8.395 Å.

In the present state of the work, the thermal analysis experiments were carried out in the isopleth [Cs$_2$O mol%]=100-2[Nb$_2$O$_5$ mol%] (Fig. 3). The results are similar to those obtained for the same section of the K$_2$O–Li$_2$O–Nb$_2$O$_5$ system [6]. The
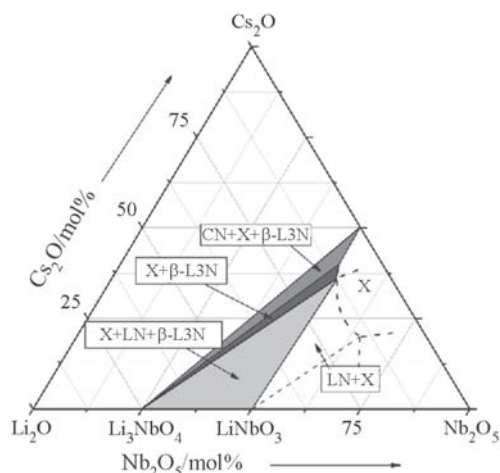
Table 1 X-ray diffraction pattern of the new phase found in the Cs$_2$O–Li$_2$O–Nb$_2$O$_5$ system

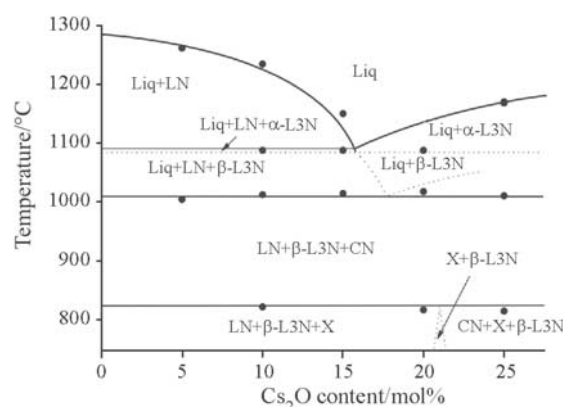| 2θ/°	I/I_0	d_{hkl}/Å	*hkl*	d_{calc}/Å
10.527	32	8.396	001	8.395
16.124	31	5.492	200	5.493
21.054	91	4.216	002	4.197
24.534	50	3.625	300	3.662
26.071	25	3.415	202	3.335
27.869	38	3.198	212	3.191
31.813	100	2.810	003	2.798
32.538	15	2.749	302	2.759
38.686	16	2.325	402	2.298
39.527	24	2.278	223	2.270

Fig. 3 Isopleth [Cs$_2$O mol%]=100-2[Nb$_2$O$_5$ mol%] with 5–25 mol% in Cs$_2$O

temperature of the peak corresponding to the highest temperature depended on the amount of Cs$_2$O content of the ceramic samples and was identified as the melting temperature of the LN phase. The crystallization limit of the LN phase is at about 16 mol% Cs$_2$O, less than one can obtain in the K$_2$O–Li$_2$O–Nb$_2$O$_5$ system, indicating that an improvement of the crystallization yield will be hardly obtained. At higher Cs$_2$O content, the Li$_3$NbO$_4$ (L3N) phase can be grown. As for the K$_2$O–Li$_2$O–Nb$_2$O$_5$ system, the other endothermic peaks were assigned to invariant reactions:

- an eutectic reaction at 1010±5°C:

  Liq.↔<LiNbO$_3$>+<β-Li$_3$NbO$_4$>+<CsNbO$_3$>
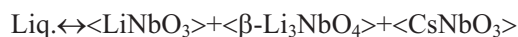
- a quasi-peritectoid reaction at 820±5°C:

  <LiNbO$_3$>+<CsNbO$_3$>↔<β-Li$_3$NbO$_4$>+<*X*>
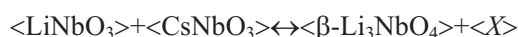
Transparent and crack free crystals with lengths of 3–4 cm could be grown starting from the composition of 10 mol% Cs$_2$O content with [Li]/[Nb]=1 located in the [Cs$_2$O mol%]= 100-2[Nb$_2$O$_5$ mol%] isopleth (Fig. 4). In the single LN phase of the crystal,
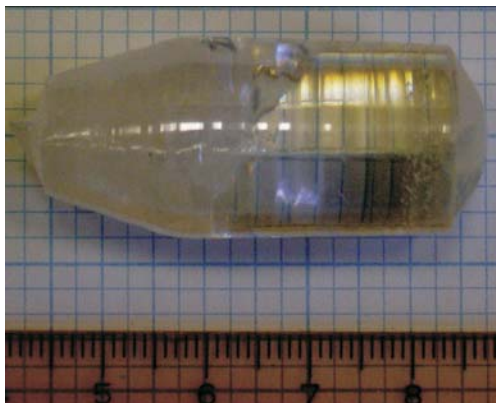

Fig. 2 Sub-solidus phase diagram of the ternary system Cs$_2$O–Li$_2$O–Nb$_2$O$_5$ at room temperature (CN=CsNbO$_3$, LN=LiNbO$_3$, L3N=β-Li$_3$NbO$_4$, X=ternary solid solution of Cs–Li–Nb oxide)

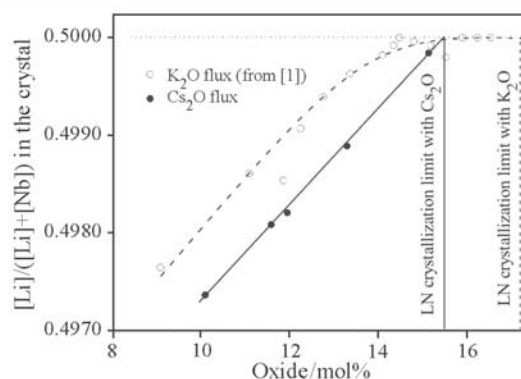**Fig. 4** LN crystal grown from 10 mol% Cs_2O containing flux

Fig. 5 Compared evolution of the composition of the solid LN phase as a function of the alkali oxide content in the flux (The crystallization limit is given by the monovariant liquid reached after complete single-phase LN crystallization)

only traces of Cs ions (i.e. 10^{-4} atom mol^{-1} or less) could be detected by chemical analysis [5], similarly to the previous results reported on the incorporation of K ions in the crystals grown from K_2O containing flux [1].

For the characterization of the crystals composition, the UV absorption edge of the samples was measured on several (00.1) cut slices perpendicular to the growth axis [7]. Since Cs ion does not enter the lattice, the [Li]/[Nb] ratio of the pure $LiNbO_3$ crystals can be determined from the UV absorption edge position measured at 20 cm^{-1} absorption coefficient, as it was reported earlier for K_2O-based flux [7]. For the most stoichiometric part of the crystals the UV edge was found at 303.6 nm corresponding to a [Li]/[Nb] ratio of about 0.9992. The [Li]/[Nb] ratio for the crystal grown from K_2O based flux was closer to 1 with a measured absorption edge of about 302.2 nm corresponding to [Li]/[Nb] ~0.9998 and for this solvent, there is a composition range (from 15.5 to 17 mol% K_2O) where crystals of constant stoichiometric composition can be grown (Fig. 5). The crystallization limit of the LN phase obtained from crystal growth experiments using cesium oxide containing flux is located around 15.5 mol% Cs_2O in good concordance with the phase diagram given in Fig. 3. Cs_2O behaves as ideal solvent similarly to K_2O, but the resulting crystal is less stoichiometric due to the lower crystallization limit in terms of oxide concentration (Fig. 5).

Conclusions

The presented work is the first known investigation of solid-liquid equilibria in the Cs_2O–Li_2O–Nb_2O_5 ternary system. We found that its behavior is very similar to that of the K_2O–Li_2O–Nb_2O_5 system. However, only quasi-stoichiometric, but good quality $LiNbO_3$ crystals can be grown using Cs_2O as a flux.

A new ternary solid solution phase was identified in the Cs_2O–Li_2O–Nb_2O_5 system in the same composition range as the so-called 'KLN' in the K_2O–Li_2O–Nb_2O_5 system.

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