Study of the phase equilibria in the ternary systems X_2O-Li_2O-Nb_2O_5 (X = Na, Rb, Cs), single crystal growth and characterization of $LiNbO_3$

Summary of the Ph. D. work

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I. Foreword

The present work is the result of a tri-lateral research among the Eötvös Lóránd University, the Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, both in Budapest, and the University Paul Verlaine (Metz, France).

I've joined this research in September 2004 as a shared Ph.D student of the University Eötvös Lóránd and the University of Metz. With an Eiffel Doctorat "co-tutelle" scholarship I've spent 15 months at a department of the University of Metz in Saint Avold (France).

Investigations in the K_2O - Li_2O - Nb_2O_5 ternary system near the existence region of lithium niobate proved that the use of K_2O as a solvent component permits the growth of stoichiometric $LiNbO_3$. The presented work extended these investigations by examining the suitability of other alkali oxides (Na_2O, Rb_2O and Cs_2O) instead of K_2O.

II. Background and objectives

Lithium (meta-) niobate ($LiNbO_3$, LN) doesn't occur in nature, the first report on its preparation and ferroelectric properties was given by Matthias and Remeika in 1949 [1]. The versatility of $LiNbO_3$ arises from the unique combination of piezoelectric, pyroelectric, electro-optical and nonlinear optical properties enabling it to be used in a wide range of applications. Most basic measurements of acoustic wave propagation, electro-optic light modulation, optical second harmonic generation, and parametric oscillation have been published between 1965 and 1967. Lithium niobate was the first material found to exhibit photorefractivity — an effect where the trapping of photogenerated charge carriers induces reversible changes in the refractive indices — which can be used for holographic image processing and information storage. Lithium niobate can be used in surface acoustic wave (SAW) filters, optical frequency converters and optical parametric amplifiers based not only on single domain bulk crystals, but also on periodically poled structures or waveguides.

Congruent composition means that the liquid and the solid phases in equilibrium have the same composition. For $LiNbO_3$ the congruent composition corresponds to the [Li] /

[Nb] ≈ 0.945 ratio. Using this starting composition in crystal growth, the segregation coefficients for both Li_2O and Nb_2O_5 are equal to 1, single crystals of good quality and uniform composition can be grown. Congruent lithium niobate (cLN) crystals can be grown easily even on the industrial scale and this is the composition used in most applications [2, 3, 4]. The drawback in the application of the cLN crystal is its high Li-deficiency leading to a large concentration of intrinsic defects. This results in a low optical damage threshold seriously limiting applications in electro-optics and non-linear optics where high energy laser radiation is required (for 10 ns pulses of 1064 nm the damage threshold is about 250 kW/cm^2). Malovichko et al. found [5] that crystals grown under appropriate conditions from K_2O containing mixtures have lower intrinsic defect concentrations. Using appropriate compositions better optical parameters and a higher optical damage threshold can be achieved yielding crystals more suitable for use in electro-optics and non-linear optics (Q-switching and frequency converters) [5, 6].

Later it was recognised that potassium itself does not enter the crystal, K_2O serves merely as a solvent and pure $LiNbO_3$ single crystal can be grown from the mixture. In this way it is possible to reach [Li]/[Nb] ~ 1 (stoichiometric composition, sLN).

By now several methods have been developed for the preparation of sLN single crystals (Li enrichment by the vapour transport equilibration method, single crystal growth from 58 mol% Li containing mixture by the continuous-refill double crucible method, the micro pulling down method for sLN fibers using stoichiometric melt, and High Temperature Top Seeded Solution Growth (HTTSSG)). Among them the composition closest to [Li] / [Nb] = 1 can be achieved by the HTTSSG method using a K_2O - Li_2O - Nb_2O_5 ternary mixture [7]. Such a solution is especially convenient for the growth of sLN crystals, since it significantly lowers the crystallization temperature determining the stoichiometry of the crystal (and the composition of the crystal is constant for a given K content range) [8, 9, 10].

The increasing need of high quality stoichiometric $LiNbO_3$ single crystals in the applications made it evident to look for other alkali metal oxide solvents beyond potassium oxide, in the hope that they can give us an easier growth process, lower crystallization temperatures or better yield of stoichiometric lithium niobate single crystals. For this end phase relations in the X_2O - Li_2O - Nb_2O_5 (X = Na, Rb or Cs) ternary systems were investigated, some of the corresponding phase diagrams were constructed, new phases were identified, growth processes were carried out and the crystals were characterized by spectroscopic methods.

III. Experimental methods

In order to understand the role of the alkali metal oxide addition in the growth of stoichiometric $LiNbO_3$ crystals several methods have been combined.

A series of X_2O - Li_2O - Nb_2O_5 (X = Na, Rb, and Cs) polycrystalline samples were prepared by solid state reactions at 1000-1200 °C (the whole amount of CO_2 was eliminated at 800 - 1000 °C) for thermal analytical, x-ray powder diffraction and crystal growth investigations. The constituent phases were assessed by X-ray phase analysis with a Philips PW 1710 diffractometer using Cu K_α radiation in the 2Θ range of 0-80° and with an INEL MPD CPS 120 diffractometer.

Thermal analytical measurements were used to determine the phase transition temperatures of polycrystalline samples in the composition range of [X] = 10-16 mol%, [Li]/[Nb] = 1 (X = Na, Rb, or Cs). The spectra were recorded with a PL Thermal Sciences 1500 Differential Scanning Calorimeter in Ar atmosphere with Al_2O_3 as the reference material. The calibration of the system was made by using 6N pure standard metals (In, Sn, Pb, Zn, Al, Ag, Au, Si).

Single crystal growth was done by the HTTSSG method from a starting composition of $[X_2O]$ = 10 mol%, $[Li_2O]$ = 45 mol% and $[Nb_2O_5]$ = 45 mol%. (During crystal growth the solution is enriched in X_2O.) The growth process was conducted further than the single $LiNbO_3$ phase crystallization limit (after the single $LiNbO_3$ phase a multi-component polycrystalline phase appeared). This way the maximum amount of the $LiNbO_3$ phase was pulled out. The constituent phases were assessed by the above mentioned Philips PW 1710 X-ray diffractometer. The X content of the samples was determined by atomic absorption analysis by a Varian SpectrAA-20 spectrometer.

The Li_2O content of different parts of the $LiNbO_3$ crystals was determined using a calibration based on the UV absorption edge position [11] which was measured by a two-beam Jasco V-550 UV/VIS spectrometer with a best resolution of 0.05 nm.

Reflection correction had to be used before the evaluation of the spectra because of the high refractive indices of the crystal. With this correction the error caused by multiple reflected light beams can be avoided.

OH^- ions which are always present in air-grown $LiNbO_3$ crystals [12] can be characterized by their vibration spectra in the infrared (IR) region. The peak intensities and full widths at half maximum in the IR spectrum are sensitive to the composition of the crystal so the OH^- vibrational spectroscopy is suitable for the composition determination of $LiNbO_3$. The spectra were recorded at room temperature by a Bruker IFS 66v/S FTIR spectrometer in the 400-7000 cm^{-1} wavenumber range with a resolution of 0.5 cm^{-1}.

The third spectroscopic method used for composition assessment in my Ph. D. work was the Raman scattering technique. With this method the vibrational modes of the chemical bonds of the matrix can be studied. For the 3m symmetry ($LiNbO_3$) the vibrational modes can be divided into three sets marked with A_1, A_2 and E. In the Raman spectrum of $LiNbO_3$ four A_1 and nine E modes can be found (the five A_2 modes are Raman inactive). These modes are characteristic for the Li - O and the Nb – O vibrations and sensitive to the stoichiometry of the $LiNbO_3$ crystals, so they can be used for composition determination. Raman measurements were carried out by a Renishaw RM1000 confocal Micro-Raman spectrometer using 633 nm He-Ne laser excitation (with a spectral resolution of about 3 cm^{-1}) and by a Labram spectrometer (Jobin-Yvon) using 633 nm He-Ne and 514.5 nm Ar-ion laser sources for the different parts of the crystals.

With the combination of the above mentioned methods – assuming that the X ion does not enter the crystal (which is true for Rb and Cs) – the compositional changes of the solution during the growth can be followed, since from the actual composition of the crystallized solid phase, the actual alkali oxide concentration of the liquid can be calculated from the pulled amount of the crystal. The real Li_2O content of the pure LN crystals can be determined by spectroscopic measurements (preferably UV absorption using the above mentioned calibration). The crystallization temperature of lithium niobate at a given composition can be deduced from the DTA measurements of the polycrystalline samples having the same composition as the actual flux from which the

crystal is growing. From the knowledge of the data triplets liquidus composition, solidus composition, and the corresponding crystallization temperature, the phase diagram – constructed by using the thermoanalytical results – can be refined.

IV. New results

1. The thermal behaviour of the X_2O - Li_2O - Nb_2O_5 (X = Rb, Cs) ternary systems was found to be very similar to that of the K_2O - Li_2O - Nb_2O_5 system, with nearly the same phase transition temperatures and constituent phases according to the thermal analytical and X-ray diffraction investigations. The limit of the $LiNbO_3$ liquidus surface was estimated to be near 16 mol% X_2O for the systems with Rb_2O and Cs_2O and with [Li] / [Nb] = 1 ratio. The ternary phase diagram of the Cs_2O - Li_2O - Nb_2O_5 system at room temperature was constructed, a new phase was found.

2. It was established that crystals with $[Li_2O]$ / $[Nb_2O_5]$ = 1 can be grown from all examined ternary systems containing between 10 - 16 mol% X_2O (X = Na, Rb, Cs). Rb_2O and Cs_2O behave as ideal solvents, since they do not enter the lattice and yield (nearly) stoichiometric $LiNbO_3$ single crystals. The crystallization temperatures are nearly the same for Rb_2O and Cs_2O containing fluxes, resulting in similar [Li] / [Nb] ratios and yields of $LiNbO_3$ crystal.

3. A new method was developed for an easy and accurate determination of the Li_2O content of undoped $LiNbO_3$ crystals close to the stoichiometric composition based on the measurement of the intensity ratio (R) of the two main hydroxyl ion vibration peaks (at 3465 and 3480 cm^{-1}) in the infrared absorption spectra. The composition can be determined from the equation $R(t) = S(t) \times (C - [Li_2O])$, where $S(t) = S_\infty - A\exp(-t/\tau)$. S_∞ represents the slope of the calibration line in thermal equilibrium, $[Li_2O]$ is the lithium oxide content of the crystal in mol%, C and A are constants, τ is the time constant describing OH^- redistribution and t is the time passed after the crystal growth. In the case of unknown thermal history (unknown t) of the crystal a simple annealing at 1000°C reconstructs the as grown state ($t = 0$).

4. It was confirmed that the FWHM of the E(TO1) Raman mode changes with the Li_2O content of the $LiNbO_3$ crystal but without correction these measurements cannot be used, as assumed earlier, for a universal composition determination of $LiNbO_3$. Using the FWHMs of the E(TO1) Raman modes excited by a He-Ne laser (633 nm) and corrected with the spectral resolution, a calibration line was determined for the z(xy)z configuration. The uncertainty of the calibration was determined as ± 0.06 mol% Li_2O content which may come from the uncertainty of the correction factor and the possible inhomogeneity of the sample surface.

5. Na was shown to be incorporated into the $LiNbO_3$ lattice with an average segregation coefficient of $k_{sol/liq}$ (Na_2O) ~ 0.2. Accordingly the phase transition temperatures for Na_2O containing polycrystalline samples are found to be higher than for Rb_2O or Cs_2O containing ones and their spectroscopic properties show changed behaviour: the UV absorption edge positions shift to longer wavelengths, the OH^- vibrational bands merge to only one asymmetric band and the Raman peaks also broaden and shift. According to normal coordinate analysis the A_1(TO1) mode is related to Nb-O vibration, while the A_1(TO2) mode mainly involves Li-O/Nb-O motions. Therefore the increase of the intensity of the A_1(TO2) mode induced by the incorporation of the Na ions into the lattice indicates that Na enters Li sites.

V. Practical application of the results

The versatility of the application of $LiNbO_3$ is well-known in the practical fields of acousto-electronics and non-linear optics and electro-optics. The optical damage threshold of stoichiometric $LiNbO_3$ is higher so it is more suitable for electo-optical and non-linear optical applications than the congruent crystal which can be grown easier. The growth difficulties justify the development of alternative preparation methods or the improvement of the existing methods. This emphasizes the importance of the growth of stoichiometric $LiNbO_3$ by the HTTSSG method not only from the K_2O - Li_2O - Nb_2O_5 ternary system but from the X_2O - Li_2O - Nb_2O_5 (X = Rb, Cs) systems as well. Using the presented phase diagrams the composition of the solution in equilibrium with a custom-tailored crystal composition can be determined. Most of the

physical parameters of $LiNbO_3$ are composition dependent. Even a small change of the composition (± 0.01 mol%) causes large differences in the properties so the determination of the Li_2O content of the crystal with the highest possible accuracy is very important. The accuracy of the composition determination – described in detail in my thesis – based on the intensity ratio of the two characteristic bands in the OH^- vibrational spectra of the near stoichiometric $LiNbO_3$ satisfies the requirements imposed by the applications.

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