Properties and defect structure of potassium lithium niobate crystal

PhD thesis

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1. Preliminaries and objects

The generation of new frequencies with existing laser sources in a wide range is an important object of laser physics. Frequency doubling, frequency mixing and optical parametric amplification can be reached using nonlinear optical materials, such as potassium lithium niobate (KLN) crystal.

Tetragonal tungsten bronze (TB) type ferroelectric potassium lithium niobate ($K_3Li_2Nb_5O_{15}$, KLN) single crystal has attractive properties for applications in nonlinear optics, electro-optics, piezoelectric devices and seems to be a promising material for frequency conversion of laser diodes. KLN can be used for nanostructured domain materials, piezo ceramics and potential terahertz applications.

According to the phase diagram, ideal stoichiometric KLN crystals do not exist; excess Nb ions on Li sites (Nb_{Li}) are required to stabilize the crystal lattice. KLN has ferroelectric properties in the composition range of 51.5 - 55 mol% Nb_2O_5. Crystals with high Nb_2O_5 content in this range show relaxor behaviour with broad phase transition temperature range and frequency dependent dielectric constant. The investigation of this crystal is the topic of present dissertation.

KLN melts incongruently and the composition of the crystal bulk grown from melt changes along the growth axis. This effect limits the use of KLN crystals in applications. Variations in the composition of KLN modify the physical properties like lattice constants, Curie temperature (T_c), refractive indices and consequently the blue second harmonic generation characteristics.

The data in the literature are often unreliable because the exact cut positions of the samples in the crystal bulk are missing. However, this information is significant due to the compositional variation. Another uncertain point is the room temperature stability region in the phase diagram of KLN crystals which resulted in contradictions in the structural models published earlier.

The purpose of my PhD work was to develop a method to determine the composition of KLN crystals. Since the chemical analytical methods did not give accurate results for the amount of K_2O and Li_2O I tried to determine the concentrations from the changes of the physical parameters of KLN crystals. For this purpose several crystal samples with different compositions were investigated and the results were compared with those measured in powder samples with known compositions synthesized by the solid state reaction method.

For the determination of the room temperature stability region of the KLN single phase X-ray diffraction and dielectric measurements of KLN ceramic samples were investigated. A combined method based on UV, infrared absorption and Raman spectroscopy as well as dielectric measurements was performed for the determination of the real crystal composition. With the aid of these results a model describing the intrinsic defects in the crystal lattice was created and tested by investigating the effects of alkali ion incorporation into KLN. The phase transition of potassium lithium niobate crystals has been studied by the analysis of the results of the dielectric measurements.

This PhD work was accomplished in the Crystal Physics Department of the Institute for Solid State Physics and Optics, Wigner Research Centre for Physics of the Hungarian Academy of Sciences.

2. Experimental methods

The temperature dependence of the dielectric constant has been measured by a dielectric constant measuring device built at the Crystal Physics Department. The crystalline and the ceramic pellets have been coated with liquid silver electrodes forming plane capacitors and measured by using a HP 4274A LCR bridge at 100 kHz.

The ferroelectric phase transition temperature, T_c was determined from the anomalous behavior of the dielectric constant during the heating cycle. The accuracy of the temperature measurement was estimated to be about ± 1 ^{o}C after calibrating our PtRh-Pt thermocouple mounted to the sample holder by measuring single crystal $BaTiO_3$ and $KNbO_3$ probes with known T_c values.

The ultraviolet and visible (190–900 nm region) absorption spectra were measured using a two–beam JASCO V550 spectrophotometer with a best resolution of 0.05 nm. Raman spectra were recorded by a Renishaw 1000B micro-Raman device using a red laser beam of 785 nm wavelength providing a resolution of 1 cm^{-1}. The infrared absorption spectra were measured by a BRUKER IFS66/v FTIR spectrophotometer with 0.1 cm^{-1} maximum resolution.

3. New scientific achievements

1. Determination of the existence field of ferroelectric potassium lithium niobate crystal

KLN ceramic samples were synthesized by the solid state reaction method. The phases in the ceramic samples have been identified by X-ray phase analyses and dielectric measurements, followed by the determination of the room tempereature stability region of the ferroelectric KLN phase. We identified the existance field of the KLN single phase in narrower limits as reported earlier in the literature. The ferroelectric KLN single phase area ended at 54 mol% Nb_2O_5 concentration. All along the solid solution field the Nb_2O_5 content was above 50 mol%, the Li_2O content below 20 mol% and the $[Nb_2O_5]/[K_2O]$ ratio higher than 5/3.

2. Determination of the composition of the potassium lithium niobate crystal

The chemical analitical investigations of the KLN crystal smaples with various compositions showed that the niobium content of the KLN crystals decreases with increasing amount of the crystallized fraction (ratio of the melt pulled out), i. e. from the top to the bottom of the crystal. As the chemical analytical method assigns only the niobium content with sufficient accuracy, for characterising the concentration of potassium and lithium other methods have to be applied. For the determination of the composition of potassium lithium niobate crystal with nondestructive methods I have investigated the KLN crystal samples with spectroscopic and dielectric measurements.

2. a. From the comparison of the results of dielectric constant measurements executed in KLN ceramic and KLN crystal samples I have determined that the niobium content of the KLN crystals decreases from the top to the bottom, in agreement with the results of the chemical analitical method. The dielectric measurements have shown that the dielectric properties of KLN are predominantly determined by the niobium content and the contribution of K/Li ratio is minor. I have observed that in the infrared absorption spectra of the OH^- vibrations the intensity ratio of the two absorption bands at 3440 and 3520 cm^{-1} (I_{3440}/I_{3520}) changes remarkably from the top to the bottom of the crystal depending on the niobium content and also on the K/Li ratio of the crystal.

2. b. After recording the ultraviolet spectra of KLN crystal samples I have observed that the UV absorption edge (defined as the wawelength for which the absorption coefficient equals to 20 cm^{-1}) is characteristic for the niobium concentration of the KLN crystal and decreases with decreasing amount of Nb_2O_5 content independently from the K/Li ratio of the crystal. The UV absorption edge position is related only to niobium stoichiometry, and reflects the presence of antisite Nb ions (Nb on Li sites (Nb_{Li})). In the Raman spectra of the KLN crystals measured in x(zz)x backscattering geometry I have found that the Raman band at $\sim$640 cm^{-1} belonging to the vibrations of NbO_6 octaheda (A_1(TO) mode) also depends only on the niobium content of the KLN cyrstal and the Raman shift of this band increases with decreasing amount of niobium.

2. c. The real composition of potassim lithium niobate crystals can be determined by the combination of the four methods mentioned above. With the results of the chemical analytical method the relationship between the UV absorption edge or the Raman band at $\sim$640 cm^{-1} (measured in x(zz)x geometry) and the niobium content of the KLN crystal can be calculated, so the Nb_2O_5 concentration of the crystal samples can be determined. On the basis of the dielectric results of KLN ceramic samples dielectric measurements can be used for the determination of the relationship between the Curie-temperature and the K/Li ratio of the KLN crystal samples at constant niobium content. From the niobium content and K/Li ratio the crystal composition can be determined.

3. Defect model of potassium lithium niobate crystal

I have presented the "alkali cation vacancy formation model" to describe the charge compensation of Nb_{Li} atoms and to estimate the amount of intrinsic defects from the concentration data. In this model the sublattice of Nb^{5+} ions and the oxygen sublattice are completely filled, K^+ and Li^+ ions do not occupy other sites, the extra amount of Nb_2O_5 enters only Li^+ sites and the charge compensation mechanism is established by different amounts of the Li (V_{Li}) and K (V_K) vacancies. The charge compensated chemical formula of <KLN-1> can be written as follows

$$(K_{3-z}V_{K_z})(Li_{2-x-y}V_{Li_y}Nb_{Li_x})Nb_5O_{15}$$

where x, y and z denote the number of antisite Nb atoms (Nb_{Li}), V_{Li} and V_K vacancies, respectively, and the charge compensation is established by the equation: $y + z = 4x$. We can calculate the amount of defects (Nb_{Li}, V_K, V_{Li}) in a KLN sample with allowed concentration. Possible values of x, y and z are:

$$0.05 < x < 0.13, 0 < y < 0.52, 0 < z < 0.2$$

These relations limit the existence field of KLN in the phase diagram with perfect agreement with the phase limits determined from X-ray diffraction investigations. On the basis of the defect model I showed that the defect concentration in the KLN crystal increases linearly with the Nb_2O_5 content and the formation of lithium vacancies is dominant. In the existence field of the ferroelectric KLN phase the defect concentration corresponds to at about 2.5-6.5% of the cation sites in the KLN crystal lattice.

4. Entering of alkali cations in potassium lithium niobate crystals

For the investigation of the alkali sites in KLN crystals and the verification of the alkali cation vacancy formation model I have investigated KLN crystals doped with alkali homologue ions: $^{6}Li^{+}$, Na^{+}, Rb^{+} and Cs^{+}, using Raman and UV absorption spectroscopy.

4. a. The Raman shift of the A_1(TO) mode belonging to the NbO_6 oxygen octahedral vibration at about 640 cm^{-1} - similarly to the UV absorption edge position - depends only on the Nb_2O_5 content both in pure and alkali homologue doped KLN crystals.

4. b. In the Raman spectra of KLN crystals phonon modes at $\sim$306 cm^{-1} and $\sim$350 cm^{-1} corresponding to K^{+} and Li^{+} ion vibrations, respectively, have been identified by Na doping and ^{6}Li isotope substitution. Raman measurements show that Na^{+} ions substitute both Li^{+} and K^{+} ions in the potassium lithium niobate crystal lattice. From a comparative study of undoped and Rb doped KLN crystals it was concluded that Rb^{+} ions incorporate only at K^{+} sites in the lattice. These results are in good agreement with the alkali cation vacancy formation model.

However the incorporation of Cs^{+} ions was found to be below the detection limit of Raman site spectroscopy. On the basis of the results of UV absorption specroscopic measurements the stoichiometry of the KLN crystals doped with Cs^+ improves as compared with the stoichiometry of undoped KLN crystals.

5. Study of the phase transition of potassium lithium niobate crystals

I have detected that the phase transition of KLN crystals depends strongly on the composition. From the temperature dependence of the dielecric constant I have assessed that the KLN crystal samples cut from the top of the crystal show relaxor behaviour while towards the bottom of the crystal the samples show more tipical ferroelectric behaviour, which can be attributed to decreasing Nb_2O_5 content, i. e. decrease of the intrinsic defect concentration.

I have observed that the maximum of the dielectric constant and the characteristic temperature of the phase transition increase the decreasing amount of Nb_2O_5 content of KLN crystals, the diffusiveness of the phase transition decreases with decreasing amount of Nb_2O_5 concentration, and a change of the slope is found at about 52 mol% Nb_2O_5 concentration. In the case of KLN crystals containing more than 52 mol% niobium the phase transition is of relaxor type.

Comparing the diffusiveness of the phase transition with the halfwidth of Raman bands characterising the vibration modes of alkali cations I have concluded that a movement of Li^+ ions (lithium vacancies) may occur during the phase transition of KLN crystals.

4. Articles related to the topic of this thesis

1. **I. Hajdara**, K. Lengyel, G. Dravecz, L. Kovács, Á. Péter, Zs. Szaller, „Spectroscopic methods for the determination of the composition of potassium lithium niobate craystals", Phys. Stat. Sol. (c) **4**, 1321 (2007)

2. **I. Hajdara**, K. Lengyel, L. Kovács, Á. Péter, G. Dravecz, Zs. Szaller „Compositional dependence and structure of hydroxyl ion defects in ferroelectric potassium lithium niobate", Ferroelectrics **369**, 98 (2008)

3. Á. Péter, **I. Hajdara**, K. Lengyel, G. Dravecz, L. Kovács, M. Tóth, „Characterization of potassium lithium niobate (KLN) ceramic system", Journal of Alloys and Compounds **463**, 398 (2008)

4. **I. Hajdara**, K. Lengyel, L. Kovács, Á. Péter and Zs. Szaller, „Effect of alkali doping on the Raman spectra of potassium lithium niobate crystals", Ferroelectrics **428**, 57 (2012)

5. Á. Péter, **I. Hajdara**, Zs. Szaller, K. Lengyel, L. Kovács, "Growth and stoichiometry of alkali ion doped potassium lithium niobate (KLN) crystals", J. Cryst. Growth (submitted)