Comparative investigation of electrophysical characteristics of ceramic and single crystal LiNbO$_3$

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Abstract. Electrophysical characteristics have been studied in ceramic and single crystal LiNbO$_3$ of congruent and near-congruent composition. The comparative study has been carried out in a wide temperature range (290-800 K). Dispersion of the real part of the dielectric constant $\varepsilon'$ has been considered. Temperature dependences $\varepsilon'(T)$ and $\sigma(T)$ have been obtained and value of static conductivity has been determined in ceramic and single crystal LiNbO$_3$ in the given temperature range. Temperature dependences of specific static conductivity $\sigma_{dc}$ have been obtained due to impedance spectroscopy data analysis. Ceramic LN conductivity has been shown to be much higher in the whole studied temperature range. Charge carriers activation enthalpy in high-temperature area (above 420 K) is $H_a = 0.88$ eV for ceramic LN and $H_a = 1.24$ eV for single crystal LN.

1. Introduction

Lithium niobate LiNbO$_3$ (LN) is a poly-functional material. It constantly attracts attention of scientists with the major in integral and nonlinear optics, quantum electronics, solid state physics [1, 2]. A substantial particularity of LN is a wide area of homogeneity on a phase diagram. A LN phase diagram particularity [2] is also strongly smoothed maxima on the liquidus and solidus curves. Thus, distect point does not coincide with stoichiometric composition. A point of congruent melting on a LN phase diagram due to different literature data varies in the range 48.3 through 48.65 mol% Li$_2$O [2–4]. Thus, nominally pure LN crystals can be obtained in the homogeneity area, which allows us to vary its properties, and thus widen its application area. LN is actively applied in both crystal and ceramic forms, for example, in acoustoelectronics and piezoelectrics. A whole class of functional and digital integrated optical circuits was created on its basis. For example, spectrum analyzers, switching matrices, microwave phase and amplitude modulators, physical quantity sensors. Thus, new synthesis methods, ways to stabilize LN mechanical, electrical and acoustic properties stays highly actual. We should note that crystal LN was studied much more intense [3–4] than ceramic one. In particular, this considers electrical conductivity mechanisms and nature [5–7]. Electrical conductivity of crystals was detected to depend strongly on [Li/Nb] cations ratio in the crystal. Existence of excess Nb$^{5+}$ ions in non-stoichiometric crystals, anti-structure defects Nb$_{Li}$, that act as deep electron traps and can form polarons at electrons capture determine LN electrical properties. The temperature range 300-450 K is highly important for application of LN crystal. Many authors have noted that this area contains a number of physical properties anomalies, including
conductivity. Influence of the anomalies on application characteristics of facilities based on LN claims detailed study.

The aim of this work is to fulfill a complex study of dielectric properties and conductivity of single-crystal and ceramic lithium niobate in a wide temperature area (290–800 K).

2. Method

Objects of this study are nominally pure congruent ([Li]/[Nb]=0.95) LiNbO$_3$ single crystals and ceramic LN obtained due to a traditional ceramic technology from fine monophasic powders with a high degree of chemical homogeneity. The powders had composition close to congruent and were synthesized by sol-gel, the method is described in detail in the work [8].

LiNbO$_3$ synthesized by sol-gel was controlled to be single phase by X-ray diffraction analysis on diffractometer Shimadzu XRD-6000. The counter speed was 1 deg/min (CuK$_\alpha$-radiation). Phases were identified due to a database ICDD (PDF 2, reliefs 2014).

Due to chemical analysis, Nb concentration in LN powder was 64.59 wt%. Li content was determined by ICP-AES on spectrometer Optima 8300. Its content was determined to be 4.56 wt%. Obtained data corresponded to chosen [Li]/[Nb] molar ratio. Specific surface area of LN powders was detected by low temperature nitrogen adsorption (BET; FlowSorbII 2300; TriStar 3020 V1. 03).

Obtained microcrystal LiNbO$_3$ powders had specific surface area $S_{sp} = 5.3$ m$^2$/g. Ceramics was prepared from these powders by annealing at 1200°C for 3h. Ceramic samples were prepared in the shape of tablets with diameter 10 mm and thickness 1 mm. Ceramic LN was quite uniform (figure 1a). As differential distribution curve shows (figure 1b), the main part of crystallites has linear size $\sim 0.2\div2$ μm.

![Figure 1. Microstructure and size distribution of ceramic LN.](image)

Nominally pure LN crystal was grown by Czochralski at air on growth plant “Crystal-2”. The plant was equipped with automatic weight control system. The system allows one to maintain constant conditions in the crystallization process. Growth was carried out from a charge synthesized with solid phase method from initial components of high purity: Li$_2$CO$_3$, Nb$_2$O$_5$, less than 10$^{-4}$ admixtures. Synthesis and granulation conditions were chosen due to differential thermal (DTA) and thermogravimetric analyses (TG) data. DTA and TGA curves were made using plant NETZSCH STA 409 PC/PG. Charge composition control was carried out by ICP-MS (ICPS, Elan-9000 by Shimadzu). Impurity cations content was not more than 10$^{-4}$ wt%.

In order to exclude influence of domain boundaries relaxation on high-temperature measurements (which is unavoidable for Z-oriented sample) X-oriented non-polar plates were cut from grown boule. The sample linear sizes were $9\times9\times1$ mm$^3$ (1 mm is a sample thickness).

Platinum electrodes were magnetron sputtered on specially prepared ceramic and single crystal LN samples. Samples were in the shape of plane parallel plates. Measurements were carried out at Solartron 1260 in the frequency range 1 Hz-1 MHz in the mode of stepwise heating. Used method provides a possibility to correctly separate contributions of different physic-chemical processes into measured
parameters and calculate values of static specific conductivity [9–10].

3. Results and discussion

The paper studies complex impedance dispersion $Z^*(\omega)$ of prepared samples of ceramic and single crystal LN in the temperature range from room to ~ 800 K. Real and imaginary parts of claimed quantities were determined from measured $Z$ and $\phi$. Obtained quantities, such as complex dielectric constant and complex impedance (admittance), characterize studied objects.

$Z''-Z'$ diagrams are qualitatively similar for all studied samples in all studied temperature range. The only relaxation process in the shape of circular arc was detected. Figure 2 demonstrates complex impedance diagrams obtained at 289 and 791 K in ceramic LN sample. Static conductivity of the sample volume ($\omega \to 0$) can be obtained from impedance hodographs, for example, by excluding polarization component. The value of sample static conductivity is $\sigma_{sv} = 1.5 \times 10^{-5}$ S/m at 289 K. It is obvious that even at room temperature ceramic LN samples has a quite high static conductivity.

An increase in temperature leads to a decrease in static conductivity. Figure 3 demonstrates hodograph obtained at 374 K for ceramic LN. The figure shows that the value of the sample static conductivity decreased to $\sigma_{sv} = 5.1 \times 10^{-6}$ S/m. Such tendency is observed to approximately 412 K, after that static conductivity starts to increase. For example, the sample static conductivity increased to $\sigma_{sv} = 7.9 \times 10^{-5}$ S/m at 791 K. As a result of complex impedance diagrams analysis we have determined values of specific static conductivity in the whole studied temperature range. The temperature dependence of specific static conductivity is demonstrated on figure 4.
Figure 4. The temperature dependence of specific static conductivity of ceramic LN.

Figure 4 demonstrates that the dependence $\sigma_0(T)$ complies with the Arrhenius law only in the high-temperature area and has a monotonous shape with activation enthalpy $H_a = 0.88$ eV. Such enthalpy is typical for bulk ion conductivity. The situation is different in low-temperature area. High values of specific static conductivity at room temperature and its decrease with an increase in the temperature is apparently connected with existence of water in the ceramic sample. Thus it is comparatively high hydrogen conductivity that contributes to electrical conductivity at low temperatures, not intrinsic ion conductivity. Water is removed with an increase in temperature, thus ceramic LN sample conductivity decreases.

Figure 5 shows temperature dependence of real part of dielectric constant. The graph demonstrates that dielectric constant dispersion in almost the entire studied range is not significant in comparison with other ferroelectrics [11–12]. And only after 700 K dielectric constant dispersion starts to increase.

Figure 5. Temperature dependence of dielectric constant in ceramic LN.
Complex impedance diagrams of studied LN single crystals show a well-resolved relaxation process of the Debye type. Figure 6 demonstrates complex impedance diagram obtained at 798 K in a nominally pure LN single crystal. Its shape is typical for all studied temperatures. We have established that static conductivity of a single crystal sample is up to $\sigma_v = 5.7 \times 10^{-5}$ S/m. Comparison of static specific conductivities of ceramic and single crystal LN samples reveals much higher values of ceramic samples.

![Complex impedance diagram](image)

**Figure 6.** Complex impedance diagrams of a nominally pure single crystal CLN with indicated frequencies (Hz) at 798 K.

Temperature dependences of specific static conductivity of a single crystal LN at frequencies 100 Hz and 1 KHz are demonstrated on figure 7. The dependence $\sigma(T)$ has two parts: high-temperature, where Arrhenius law is well executed ($H_a = 1.28$ eV), and a low-temperature one. Here the dependence $\sigma(T)$ complies with the Arrhenius law not quite precise, however averaging yields values around 0.58 eV. Such activation enthalpy values are characteristic of impurity conductivity. Conductivity of a single crystal sample switches from impurity type to intrinsic type with an increase in temperature.

![Temperature dependence](image)

**Figure 7.** Temperature dependences of specific static conductivity of a single crystal LN.
We have calculated the value of specific static conductivity of LN single crystal volume from complex impedance hodographs and obtained a dependence $\sigma(T)$ (figure 8). Comparison of temperature dependences of specific static conductivity in ceramic and single crystal LN samples revealed much higher value for ceramic sample in the whole studied temperature range. Charge carriers activation enthalpy is lower in ceramic sample (0.88 eV) than in single crystal sample (1.24 eV). Ceramic LN is a polycrystal with a great number of grains, it has a developed system of grain boundaries which actually are one big macroscopic defect (figure 1). Unlike single crystals, ceramic LN has a substantially greater amount of free ions due to a much more defective structure. Thus, polycrystal ceramic sample has a greater ionic conductivity, than single crystal sample, despite the fact that the latter is more structurally perfect.

Figure 8. Temperature dependences of specific static conductivity of a ceramic LiNbO$_3$ and congruent single crystal LiNbO$_3$.

4. Conclusion
This paper considered complex study of dielectric properties of ceramic LiNbO$_3$ and single crystal CLN. Values of specific static conductivity were determined in the temperature range 290-800K. Conductivity of ceramic sample was shown to be much higher than that of single crystal sample in the whole range of studied temperatures. Charge carriers activation enthalpy is lower in ceramic LiNbO$_3$ sample ($H_a$ =0.88 eV) than in single crystal LiNbO$_3$ sample ($H_a$ =1.24 eV). Dielectric constant dispersion is insufficient in the whole studied range, its increase starts only after 700 K.

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Declaration of interests.
Author declare no conflict of interests.
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