

# Dielectric properties of lithium niobate single crystals doped with gadolinium

M N Palatnikov<sup>1</sup>, N V Sidorov<sup>1</sup>, V A Sandler<sup>2</sup>, K Bormanis<sup>3</sup>, I Smeltere<sup>3</sup>

<sup>1</sup>Institute of Chemistry, Kola Science Centre RAS, Apatity, Murmansk Region, Russia

<sup>2</sup>Ivanovo State University, Ivanovo, Russia

<sup>3</sup>Institute of Solid State Physics, University of Latvia, Riga, Latvia

E-mail: ilze.smeltere@cfi.lu.lv

**Abstract.** In this paper dielectric properties of  $\text{LiNbO}_3\text{:Gd}$  single crystals at temperatures  $\sim 290\text{--}490$  K at narrow frequency range ( $0.5\text{--}10^6$  Hz) are presented. The influence of growth conditions was also investigated. The anomalies on dielectric plots depend on the development of the micro- and nano-domain structure.

## 1. Introduction

Lithium niobate  $\text{LiNbO}_3$  (LN) crystals have been widely used for tailoring optical and piezoelectric devices. They are used in many commercial applications however the intrinsic defects associated with the structure and growth conditions influence the properties of this material. A number of anomalies of conductivity, optical, dielectric and pyroelectric properties of lithium niobate crystals within a temperature range of  $300\text{--}400$  K has been observed by different authors [1-8]. A super-structural sub-lattice of clustered defects formed at the cation sub-lattice of rare earth elements REE-modified LN crystals is observed to have steps of the size of a few lattice translation periods [9]. There are clusters formed close to the defects ( $\text{Nb}_{\text{Li}}$ ) having a pattern with periodic nano-size fractal structures of steps between  $1\text{--}2$  nm [10].

In the present work the influence of gadolinium Gd on the observed dielectric anomalies in  $\text{LiNbO}_3$  single crystal was investigated.

## 2. Results and discussion

LN single crystals were grown under stationary and non-stationary conditions. The dielectric dispersion of  $\text{LiNbO}_3\text{:Gd}$  single crystals was investigated. Measurements were performed at temperatures  $\sim 290\text{--}490$  K within narrow frequency range ( $0.5\text{--}10^6$  Hz). Short periodical temperature oscillations at crystal – fusion phase boundary within the crystal growth promotes the forming of contrary polarized domains [11-17]. Domain boundaries are characterized by a complex structure. The examination of lithium niobate crystals containing gadolinium ( $\text{LiNbO}_3\text{:Gd}$ ) has revealed formation of regular micron-scale domain structures (RDS) characteristic for this kind of crystals (Fig. 1).



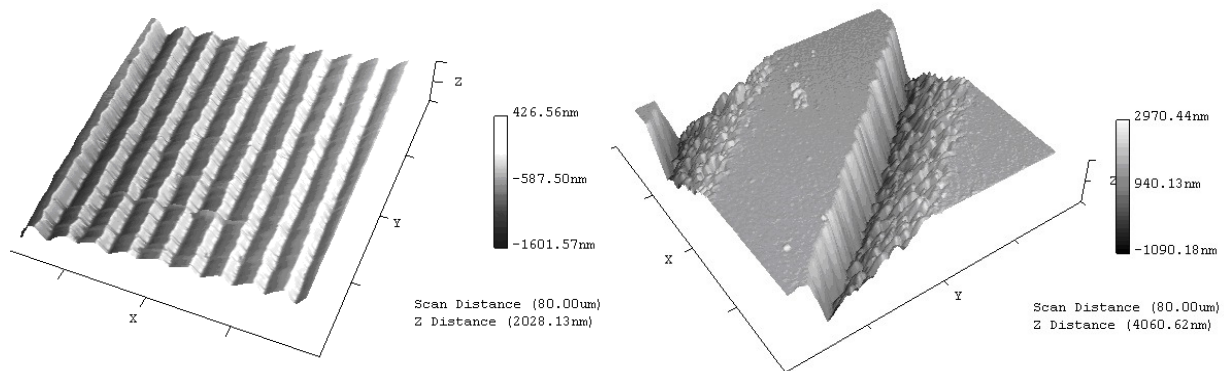


Fig. 1. Regular domain structure in non-stationary grown LiNbO<sub>3</sub>:Gd [Gd=0.44 wt%] single crystal. Image is taken with Atomic force microscope Nano R2™

There is an anomaly on the dielectric permittivity plot  $\epsilon'_{33}(T)$  observed at around 330-380 K. Dielectric permittivity decreases with increasing frequency and disappears at  $f \geq 10$  kHz. Dielectric dispersion at low frequencies follows Debye equation. Fig. 2 shows the Cole-Cole diagram for LiNbO<sub>3</sub>:Gd single crystal.

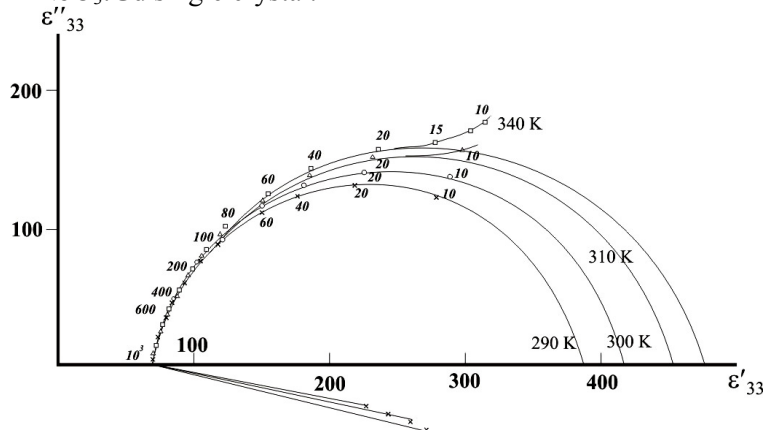


Fig.2. Cole-Cole diagram for LiNbO<sub>3</sub>:Gd [Gd=0.44 wt%, z-orientation] single crystal in the temperature range from 290 to 400 K. Frequencies are shown in Hz at curves

Monodispersion is located at temperatures 290-340 K in the frequency range 10 Hz to 10 kHz and can be described with an equation (1):

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (1)$$

where  $\epsilon^*$  is the complex dielectric permittivity,  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the dielectric permittivity,  $\omega$  – the angular frequency,  $\tau$  – relaxation time.

The dielectric dispersion nature is changed with increasing temperature. These changes appear as linear areas on the Cole-Cole diagram at low frequencies. These linear areas become more pronounced and extended with increasing temperature. Relaxation becomes longer in time. Dielectric dispersion following the equation (1) is suppressed above 410 K (Fig. 3). It means that there are two dispersion processes present at 290~410 K: Debye processes (I) and the linear area at lower frequencies (II). When temperature exceeds 490 K only the process (II) appears on Cole-Cole diagram.

The depth of dispersion does not change essentially while increasing temperature from 290 K to 340 K. Further increase in temperature above 340 K (even 4 K) drastically decreases the depth of dispersion.

LiNbO<sub>3</sub>:Gd crystal is associated with one Debye relaxation process in temperature range from 290 K to 340 K with a relaxation time  $\tau \sim 2.5 \cdot 10^{-2}$  s at room temperature.

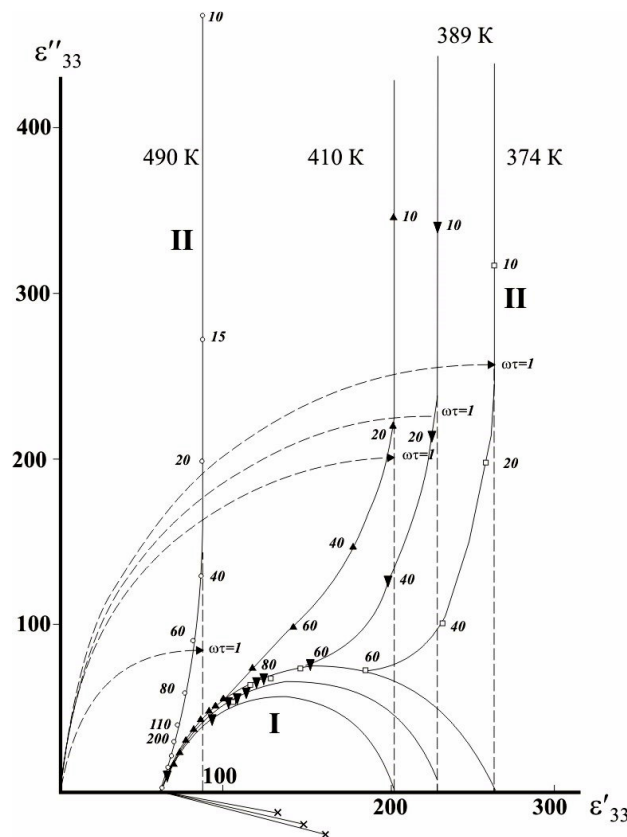
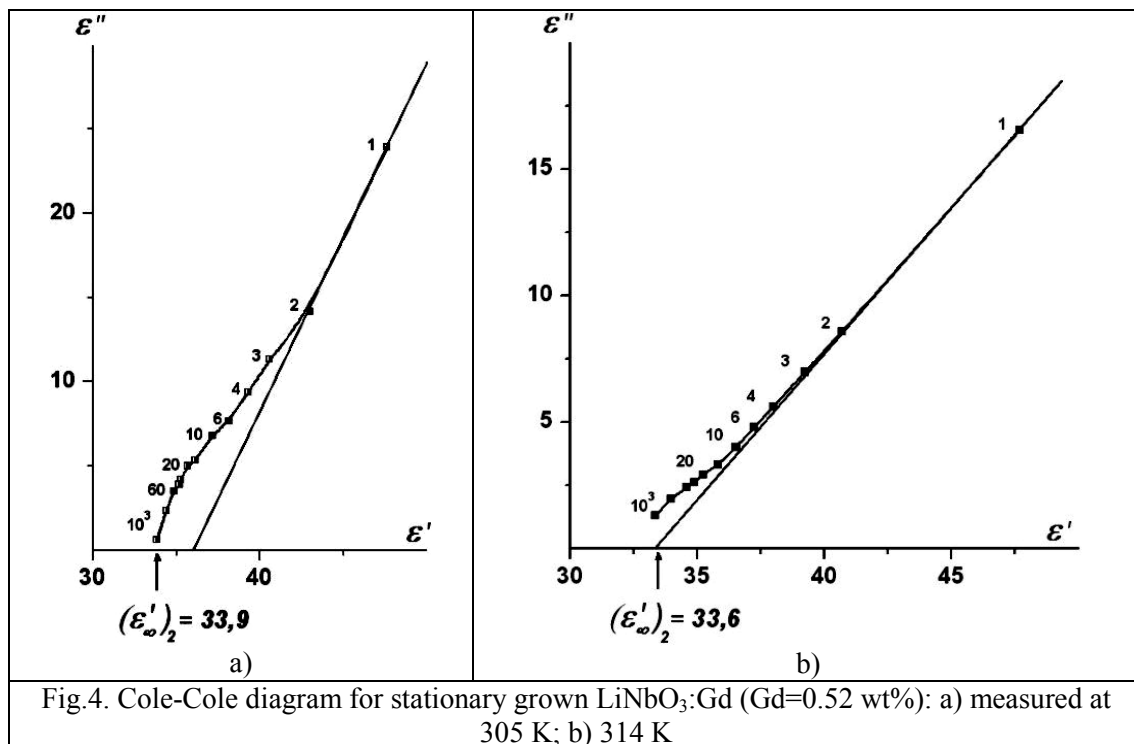


Fig.3. Cole-Cole diagram for LiNbO<sub>3</sub>:Gd [Gd=0.44 wt%, z-orientation] single crystal in the temperature range from 374 to 490 K. Frequencies are shown in Hz at curves

The Debye process (I) disappears after holding the sample at 340 – 350 K for 4 hours. The investigation of dielectric dispersion under different voltage (0 – 10 kV/cm) in bias field shows decrease of dispersion depth. At the same time there is no evidence for the Debye nature change. The observations mentioned above allow us to assume that the anomalies are caused by the interaction of spontaneous polarization relaxation and defect relaxation (associated with impurity of Gd<sup>3+</sup>) with periodic domain or nanostructure boundaries. Constant electric field leads to domain growth and consolidation of domains causing the decrease of dispersion depth. Stationary grown LiNbO<sub>3</sub>:Gd (0.52 wt%) without developed micro- and nano- domain structure was also examined. Figure 4a shows two relaxation processes at T=290 K in frequency range of 1 Hz to 1 kHz. The first is Debye relaxation, the second emerges as a straight line associated with the static conductivity of the sample. The Debye process disappears instantly with a slight rise in temperature (Fig. 4b). Numerically dispersion depth is much higher for samples grow non-stationary. Smaller dispersion depth is the evidence of the unipolarity of a crystal.



### 3. Conclusions

Dielectric properties of stationary and non-stationary grown LiNbO<sub>3</sub>:Gd single crystals at temperature ~ 290–490 K in narrow frequency range (0.5–10<sup>6</sup> Hz) were investigated. Interaction of spontaneous polarization relaxation and defect relaxation with periodic domain or nanostructure boundaries causes the low-frequency dielectric dispersion. The dispersion depth is defined by evolution of micro and nano domain structure.

### 4. References

- [1] Kuzminov Y.S. 1987 *Moscow Pub: Science* 264
- [2] Kamencev V P, Nekrasov A V, Pedko B 1983 *Physics Series USSR Press* **47** 791
- [3] Rotberg M B, Novik V K, Gavrilova N D 1969 *Crystallography* **14** 938
- [4] Pedko B, Lebedev E V, Kislova I L, Volk T L 1998 *SPP* **40** 337
- [5] Blistanov A A, Makarevskaya E V, Geraskin V V 1978 *SPP* **20** 2575
- [6] Bagdasarov H S, Bodanov M J 1987 *SPP* **29** 2380
- [7] Belabaev K G, Gabriellan V T, Sarkisov B H 1973 *Crystallography* **18** 198
- [8] Voskresensky V M, Starodub O R, Sidorov N V, Palatnikov M N, 2011 *Crystallography* **56** 26
- [9] Pedko B, Rudyak V M, Shabalin A L 1990 *Physics Series USSR Press* **54** 1154
- [10] Palatnikov M N, Sherbina O B, Sidorov N V, Bormanis K 2010 *Crystallography* **55** 859
- [11] Palatnikov M N, Sandler V A, Sidorov N V, Guryanov A V, Kalinnikov V T 2000 *SPP* **42** 1456
- [12] Palatnikov M., Shcherbina O, Biryukova I, Sidorov N 2008 *Ferroelectrics* **374** 41
- [13] Palatnikov M., Shcherbina O, Kazakov A A 2008 *Inorganic materials* **44** 360
- [14] Naumova I I 1994 *Crystallography* **39** 1119
- [15] Naumova I I, Glinko O A 1996 *Crystallography* **41** 749
- [16] Naumova I I, Evlanova N F, Gilko O A 1997 *J.Cryst.Growth.* **181** 160
- [17] Ming N, Hong J, Feng D J. 1982 *Mater. Sci.* **17** 1663