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Anomalous behaviour of periodic domain structure in Gd-doped LiNbO$_3$ single crystals

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Abstract. Atomic force microscopy studies of etching patterns, stability of regular domain structure, and anomalies of electrical characteristics in the 300 – 385 K range of a series of Gd-doped lithium niobate single crystals grown under equal conditions are reported.

1. Introduction
Studies of nonlinear crystals activated by rare earth ions to combine laser and nonlinear properties are being insistently developed. Recent success in this field of laser physics is related to applications of hetero-structured semiconductor diodes for pumping and advancement of technologies for active highly nonlinear crystals specified by high thresholds of optical damage.

Application of active nonlinear crystals with regular domain structure (RDS) the studies of which are recently being developed opens new opportunities for efficient auto-transformation of frequency whenever laser generation and quasi-synchronous nonlinear transformation emerge in the crystal. Lithium niobate single crystals activated by different rare earth ions and specified by growth RDS are amongst the most prospective active nonlinear materials.

A number of anomalies of physical properties emergence of which is rather ambiguous are observed in lithium niobate in the practically significant range of temperature (300 – 385 K). Since such anomalies may straight affect the operational parameters of a lithium niobate device, a considerable number of studies [1 – 9] have been devoted to them.

The domain structure, static and dynamic piezoelectric and dielectric properties of rare-earth doped lithium niobate crystals within the particular range of temperature over a wide frequency interval have been studied to obtain additional experimental data about the nature the observed anomalies.

2. Experimental
The Gd-doped lithium niobate single crystals were grown in platinum crucibles of 65 mm diameter by Czochralsky’s technique under atmospheric conditions on the appliance “Kristall-2” at a small axial thermal gradient (2-4 degrees per cm) in the direction of the polar axis (z-cut), a constant rate of rotation (16 rev/min) and displacement (0.8 mm/h) the growth rate being 1.08 mm/h. The process was stopped by reaching the mass of crystal about 100 g (no more than 12 % of the total mass of melt). All the grown crystals had a flat front of growth and the same size: diameter 30 mm, the length of the cylindrical part $L_c = 30$ mm. The crystals were not subject to coercive domain orientation.
Samples for studies of electrical properties were prepared in the form of parallelepipeds of the size 5×5×(0.6-1) mm with orientation normal to axes x, y, z. Platinum electrodes were deposited on the flat surfaces by magnetron sputtering in Ar environment at pressure 10⁻³ torr after ion cleansing.

The dielectric properties were studied by amplitude-phase-frequency detection technique in the frequency interval of 1 Hz – 1 MHz. Thermal dependences of the piezoelectric modulus \(d_{33}\) were obtained at uniaxial load of \(z\)-oriented samples the induced charge being measured by an electrometric voltmeter.

Surface morphology of the crystals was studied at high accuracy and high resolution by an SMM-2000 scanning multi-microscope (produced at the “Proton-MIET” factory, Zelenograd, Moscow) operated in the soft contact mode of atomic force microscopy with Veeco (USA) MSCT-AU cantilevers. The cantilever – a 200 μm long, 20 μm wide and 0.6 μm thick silicon nitride console beam the end of which has a silicon nitride needle with tip of the diameter of 100 Å is brought to the sample surface. A small pressure the force of which within the range of 1 – 10 pN does not destroy the atomic structure of the sample is made on the surface as the needle tip touches it bending the cantilever beam by merely 10⁻²⁻²Å. The bend of the cantilever is detected by deviation of laser beam reflected from it with the accuracy of 0.05 Å. After that the sample is scanned sustaining a constant bend of the cantilever at the expense of correcting the level of the other end of the lever fixed to a piezo-engine. The vertical resolution of the profile under the SMM-2000 microscope is 0.05 – 0.1 Å, the lateral – between 20 and 50 Å (2-5 nm). The “Scan Master” software of the microscope presents on the display either two-dimensional picture the colours corresponding to heights of the dots or 3D images with virtual illumination making it similar to pictures seen in electron or optical microscopes.

3. Results and discussion

Examining the etching pattern from the rotational growth figures (figure 1) it was concluded that RDS is formed mainly in the upper part of the \(LiNbO_3:Gd\) crystals (up to \(\frac{2}{3}\) of the cylinder length). The absence of RDS in the lower part of crystals is likely due to the change of thermal conditions with the level of the melt getting lower. A similar RDS has been observed in lithium niobate crystals with \(Y^{3+}\), \(Dy^{3+}\), and \(Nd^{3+}\) dopants [10]. Admixture of rare earth elements facilitates formation of RDS because of uncompensated charge, large ion radius (\(Gd^{3+} - 0.94\), \(Y^{3+} - 0.97\), \(Dy^{3+} - 0.88\), \(Nd^{3+} - 0.99\)), and effective distribution coefficient \(K_{eff} < 1\).

Distribution of the \(Y^{3+}\) admixture has been studied in rotational growth figures of \(LiNbO_3:Y\) single crystals [11]. By measuring distribution of the admixture along the normal of domain boundaries it was found that domains are formed near yttrium concentration maximums and minimums. A similar picture should be observed in case of other rare earth elements having the same cation charge and ion radius value close to that of yttrium. At the ferroelectric phase transition in the crystal the charge of admixture is not completely screened. Therefore, the distribution of admixture not being homogeneous is equivalent to heterogeneous distribution of the charge and, consequently, to heterogeneous intrinsic field and formation of domains with the opposite polarity.

The temperature curves of real dielectric permittivity \(\varepsilon'_{33}(T)\) were studied at different fixed frequencies in samples of Gd- and Tm-doped lithium niobate crystals with RDS. A considerable anomaly of \(\varepsilon'_{33}(T)\) intensity of which decreases with the frequency and practically disappears at 10 kHz was observed in the 330-380 K range of temperatures (figure 2). The curves were obtained at heating, and it is important that intensity of the anomaly drops off by more than an order of magnitude at consecutive heating-cooling cycles.

The obtained data allow to assume the observed anomalies being of relaxor nature. Results of the measurements of dielectric dispersion are illustrated in figure 3 showing the Cole-Cole diagrams of the \(LiNbO_3:Gd\) crystal at first heating (294.8 K) and after heating cycle at 344 K (0 h, 1 h, or 2h samples were held at 344 K). As follows from the diagrams, within the 1 Hz – 1MHz frequency range the dielectric dispersion in \(LiNbO_3:Gd\) is due to a single Debye relaxation process the characteristic time
Figure 1. Atomic force microscopy image (size $11.5 \times 10 \mu m$, height span $700 \text{ nm}$) of the regular domain structure of LiNbO$_3$:Gd (0.44 % by mass) taken on microscope SMM-2000.

Figure 2. Dielectric permittivity of LiNbO$_3$:Gd (0.44 % by mass, z-direction) crystal as function of temperature at frequencies $10^2$, $10^3$, and $10^4$ Hz.

of which is $\tau \sim 2.5 \cdot 10^{-2}$ sec at room temperature. Heating the sample up to temperatures not exceeding 340 K does not change perceptibly the dispersion and dielectric permittivity showing dependence of the time of dielectric relaxation that follows Arrhenius law.

The anomalies of thermal behaviour and the specific slow evolution of dielectric properties, features of dielectric dispersion, the values of relaxation time constants and activation energy (at least in the range of temperatures where conductivity and relaxation time follow Arrhenius law), and the type of domain structure suggest that the observed low-frequency dielectric relaxation is due to point defects (related to the rare earth admixture) interacting with the regular domain boundaries of the primary polydomain crystal.

Figure 3. Cole-Cole diagrams of LiNbO$_3$:Gd (0.44 % by mass, z-direction) crystal at different measurement cycles: at first heating (294.8 K) and after heating cycle at 344 K (0 h, 1 h, or 2h samples were held at 344 K).

Figure 4. Atomic force microscopy image (size $5 \times 5 \mu m$, height span $400 \text{ nm}$, microscope SMM-2000) of the domain structure in samples of the lower part of LiNbO$_3$:Gd (0.44 % by mass) single crystal.
As a rule, the growth RDS were not observed in the lower part of our lithium niobate single crystals containing rare earth admixtures. In this part of the crystals etching patterns revealed a domain structure usually found in ostensibly pure single crystals (figure 4). Obviously, this has to do with the features of the thermal conditions at the crystallization front being changed as the level of melt lowers in the process of crystal growth. It has to be noticed that $\varepsilon_{33}(T)$ curves of such crystals are very close to similar curves of z-cut samples of ostensibly pure lithium niobate crystal.

Thermal behaviour of static and dynamic piezoelectric effects were examined to study the thermal stability of the domain structure in RDS samples. A possible weak natural unipolarity being neglected it should be assumed that a macroscopic piezoelectric effect is absent in polydomain samples. Maximum values of the macroscopic piezomodulus are expected in the single domain state far from the Curie point. The unipolarity of a particular sample may be evaluated by experimentally measured value of its piezomodulus. Direct measurements of the static macroscopic piezomodulus $d_{33}$ and its thermal behaviour are presented in figure 5.

$$d_{33} = 10^{-12} \text{ C/N}$$

The experimental results attest that $d_{33}$ is small at heating samples to temperatures $T < 340 K$ where it is likely due to a weak natural unipolarity while in the range of the observed anomalies of dielectric properties and conductivity there is a sharp increase of the $d_{33}$ piezomodulus up to values close to those characteristic of ostensibly pure single domain crystal. The normalized signal of piezoelectric resonance thickness oscillations (z-direction) as function of frequency in two regions of temperature corresponding to different domain structure of the sample are also shown in figure 5. As in case of the static measurements, the intense maximums of the signals at resonant frequencies appeared abruptly near $T_0 \sim 340 K$ at heating and stay irreversibly during thermal cycles.

The sharp increase of the $d_{33}$ piezomodulus in LiNbO$_3$:Gd crystals is accompanied by substantial change of the near-surface etching micro-profile related to RDS. A micro-profile with a distinct direction revealing the fine features of the RDS is well pronounced in a sample of weak natural unipolarity and being examined before thermal measurements (figure 6a). Such a micro-profile is practically absent in the sample etched immediately after dielectric measurements (at $T>340 K$) the

Figure 5. Piezomodulus $d_{33}$ of LiNbO$_3$:Gd (0.44 % by mass, z-direction) crystal as function of temperature; inserts – signals of piezo-resonance at $T < T_0$ and $T > T_0$. 

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piezomodulus of which has been measured to be $d_{33} \approx (11-12) \cdot 10^{-12} \text{C/N}$ (figure 6b). The experiment is a direct proof of the rearrangement of domain structure in LiNbO$_3$:Gd crystals at temperatures close to $T_0$.

**Figure 6.** AFM (SMM-2000) image of the near-surface etching profiles of LiNbO$_3$:Gd (0.44 % by mass, z-direction) crystals (etched at room temperature): a – before heating (size $17 \times 16 \mu\text{m}$, height span $500 \text{nm}$, $d_{33} \approx 0.2 \cdot 10^{-12} \text{C/N}$); b – after measuring of electrical parameters (size $17 \times 14 \mu\text{m}$, height span $200 \text{nm}$, $d_{33} \approx (11-12) \cdot 10^{-12} \text{C/N}$).

### 4. Conclusions

Hence, the experimental results support the assumption that originally polydomain Gd$^{3+}$-doped lithium niobate crystals have a fairly unstable domain structure. At heating up to temperature $T_0 \sim 340$ K they exhibit anomalous thermal behaviour point to the domain structure being transferred to a strongly unipolar state with properties close to the single domain condition. The state is lasting at temperatures $T > T_0$ and quasi-stable at lower temperatures.

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