

# PARAMAGNETIC DEFECTS AS PROBES FOR THE STUDY OF FERROELASTIC PHASE TRANSITION IN LITHIUM NIOBATE AND LITHIUM TANTALATE UNDER HIGH PRESSURE

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It was found by optical polarization microscopy and the EPR study that lithium niobate and tantalate crystals undergo irreversible lattice changes under anisotropic hydrostatic compression. Regions having different cell orientations were registered. The observed changes were explained in terms of “strain switching” of ferroelastic domains. Possible sequence of phase transitions in these crystals ( $Pm3m \leftrightarrow R\bar{3}c \leftrightarrow R3c$ ) and the symmetry of the condensed soft modes ( $R_{25}$  and  $\Gamma_{15}$ , correspondingly) were obtained by the analysis of the Gibbs free energy under external pressure.

*Keywords:* EPR;  $\text{Cr}^{3+}$ ; Lithium niobate; Lithium tantalate; High pressure

## 1. INTRODUCTION

Lithium niobate (LN) and lithium tantalate (LT) crystals at the atmospheric pressure undergo a phase transition from the ferroelectric phase  $R3c$  to the paraelectric phase  $R\bar{3}c$  at the temperatures about 1400–1485 K and 800–930 K respectively. At the very high pressure about 35 GPa a phase transition to the cubic structure was registered [1]. A transformation of luminescence spectra of  $\text{Cr}^{3+}$  in LN and LT was recently studied in details at 2–15 GPa [2–11].

This contribution reports about our study of LN, LT and ruby crystals after the compression in a high pressure apparatus of lens type filled with graphite powder and heated by an electric discharge through the graphite (Fig. 1). Paramagnetic probes as well as x-ray structural analysis, and optical polarization microscopy were used to register the lattice transformations.

## 2. EXPERIMENTAL CONDITIONS

The axial compression force  $F$  ranged from 15 to 625 kN, and this created in the working volume filled with graphite powder as a transmitting medium a pressure of about

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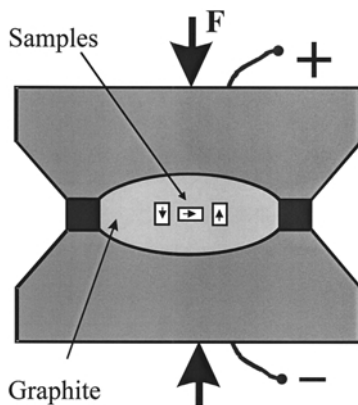


FIGURE 1 High-pressure lens-type chamber.

0.1–1.8 GPa. The steady load was applied for between 0.5 and 15 min. The experiments were carried out both at room temperature without heating, and with heating by an electric discharge through the graphite ( $J_{\max} \sim 25$  kA,  $t_h = 800$   $\mu$ s,  $T_h \sim 800$ –1000 K). The samples were optically transparent, uniformly colored  $x$ ,  $y$ , and  $z$  cut crystal plates with dimensions up to  $3 \times 4 \times 2$  mm. They were placed at the center of the working volume with the  $z$  axis parallel or perpendicular to the axial  $F$ .

### 3. RESULTS

The EPR and optical spectra of typical paramagnetic probes, like  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  are well investigated and characterized [12–15]. Main axial centers of these defects have  $z$ -axis parallel to trigonal crystal axis ( $z \parallel c$ ) and no other defects in the neighborhood, whereas distorted low-symmetry satellite centers consist of the impurity ion and of intrinsic defects present in these nonstoichiometric crystals. Studied LN, LT samples were single-domain or with  $180^\circ$  domains, which are not distinguishable by our methods.

No effect was found in all samples for  $F \perp z$  with or without heating. However, for a configuration with  $F \parallel z$  at loads above 30 kN without heating and in all the experiments with heating some bands forming equilateral triangles in the plane perpendicular to the  $z$  axis appeared on the crystal surfaces. They were observed in LN and LT samples, but not in ruby. New EPR lines in the spectra of paramagnetic probes were registered in these samples. Their intensities  $I_i$  were comparable with the intensities  $I_1$  of known EPR lines (center No 1,  $z_1 \parallel c$ ) before compression (Fig. 2). The position of new lines were described by assuming that the samples after the compression contain three additional centers (No 2, 3, 4) with the same parameters of spin-Hamiltonian as No 1, but with different orientation of center axes  $z_i$  ( $i = 2, 3, 4$ ). The Euler angles  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$  of the coordinate systems relative to  $x$ ,  $y$ ,  $z$  were  $\alpha_2 = 90^\circ$ ,  $\alpha_3 = 210^\circ$ ,  $\alpha_4 = 330^\circ$ ,  $\beta_i = -103^\circ$ ,  $\gamma_i = 90^\circ$ .

Such reorientations of center axes cannot be explained by a relocation of intrinsic defects. Since similar pictures were observed for all probes, a conclusion was been made that regions with different cell orientations appeared under these conditions. The achieved temperatures were above 900 K, since recharging of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  was observed, but below melting points. The study of samples by polarization optical microscope and x-ray analysis confirmed the presence of macroscopic areas with rotated cells.

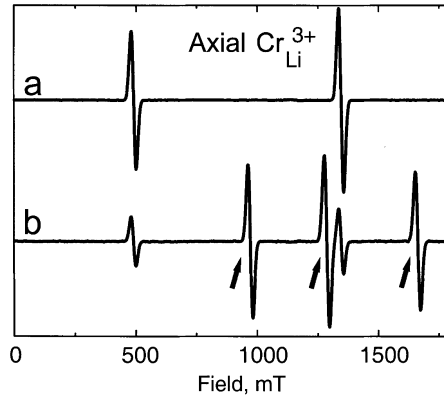


FIGURE 2 The EPR spectra of  $\text{Cr}^{3+}$  in LN before (a) and after (b) compression. Appeared lines are indicated by arrows.

4. DISCUSSION

The observed changes in the lithium niobate and tantalate lattices cannot be explained by re-crystallization in selective directions from the liquid phase, since they are observed at room temperature. Slips under anisotropic pressure or at a pressure above the yield stress also should be excluded of a consideration, since in that case the paramagnetic center axes do not change their orientations, but remain parallel to the  $z$  axis (except for a negligible fraction which lies in the slip plane).

In our view, the most convincing explanation of the effect is to relate it to the existence in these crystals of a cubic phase at high pressures only.

With the usual method of growing crystals at atmospheric pressure, the samples are obtained in the  $R\bar{3}c$  phase. The  $C_3$  or  $z$ -axis is directed along body diagonal of elementary cell rhombohedra (elongated cub). After cooling to room temperature the samples split up

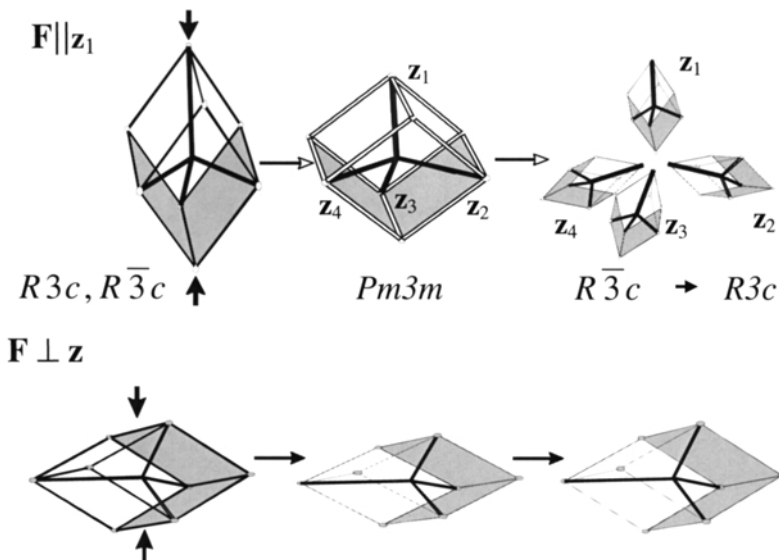


FIGURE 3 Lattice transformation under anisotropic compression.

into ferroelectric  $180^\circ$  domain crystals ( $R\bar{3}c$  phase). Under anisotropic hydrostatic compression applied along elongated axis (Fig. 3) the rhombohedra transforms into a cub (phase transition into cubic phase). A removal of the compression leads to reversal phase transition from cubic to trigonal phase; however since there is no preferable condition for the crystal distortion along four body diagonals, the samples split up into four domains.

Heating the samples (by a current pulse or otherwise), like the hydrostatic component of the anisotropic compression, lowers the barriers between the domains and facilitates this transformation.

The theoretical analysis of the Gibbs free energy under external pressure has shown a possibility for a sequence of phase transitions in LN and LT crystals with the symmetry of condensed soft modes:  $Pm\bar{3}m \leftrightarrow R\bar{3}c$ , “rotational” mode  $R_{25}$  (ferroelastic phase transition);  $R\bar{3}c \leftrightarrow R\bar{3}c$ , polar mode  $\Gamma_{15}$  (ferroelectric phase transition). The applied high pressure under heating switches a strain of ferroelastic domains just as electric fields switches a polarization of ferroelectric domains. The observed difference of the transformation for samples placed perpendicular or parallel to lens axis proves evident anisotropy of hydrostatic compression in the high pressure apparatus.

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