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The Role of Jahn–Teller Ions in the Creation of Domain Structures in Lithium Niobate

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Abstract—Using tightly focused laser beams, features of space charge fields (~107 V/m) are studied through the photoionization of doped Jahn–Teller Fe^{2+} ions in $LiNbO_3$ single crystals. These fields can be used for selective formation of the inverse domain state following the additional application of a field with a strength below the coercive field. The characteristics of laser-induced domains and periodic domain structures are studied by laser-acoustic means.

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INTRODUCTION

Over the last decade, the use of oxide ferroelectrics in devices and instruments of opto- and acousto-electronics has grown rapidly, due to the development of new techniques for creating periodic domain structures (PDSes) with periods of 0.3 to 20 μm. Earlier, the most widely used technique for creating PDSes in ferroelectrics of the lithium niobate type was the local electric repolarization of single-domain samples. Since it is quite difficult to create the structure of periodic electrodes in specified intervals on the surfaces of crystals, a new technique has been developed that involves creating spatially periodic gradients of photoinduced electric field E_{ph}, obtained by irradiating the surface of a crystal with an interfering laser beam, and applying uniform electric field E_{dep} opposite spontaneous polarization field E_s. When the sum of fields E_{ph} and E_{dep} exceeds field E_s, we have local repolarization in maxima E_{ph} with a period equal to the one of the interference of the optical beams.

When a PDS forms, it is desirable to reduce the coercive field; this can be done in two ways. In the first, field E_s can be reduced during the transition from congruent samples with a high deficit of Li ions relative to the stoichiometric composition. However, stoichiometric crystals have yet to be grown industrially and are fabricated only in individual laboratories; we therefore normally dope the charge using such ions as Mg, Zn, and Er with the highest concentrations of ~1–3 at % in order to reduce E_s. In this respect, doping lithium niobate crystals with Jahn–Teller ions (Cr^{2+}, Mn^{3+}, Fe^{2+}) [1–3] with concentrations on the order of 10^{-5} to 10^{-3} at % is of the greatest interest. The considerable reduction in the required concentration of dopants is due to the presence of large quadrupole moments of Jahn–Teller ions directed opposite field E_s. Total field E_{ZZ} of all quadrupole moments of a Jahn–Teller ion creates partial compensation for E_s. Since the domain boundaries in oxide ferroelectrics have a number of features that affect nonlinear elastic and optical characteristics, this has stimulated intense study of them [4–6]. In [7], we studied features of simpler boundaries of the head-to-head and tail-to-tail types; however, aspects of the formation of a spatially periodic photoinduced field were not considered.

EXPERIMENTAL

In this work, the effect Jahn–Teller ions have on the formation of domains and PDSes with domain boundaries of the head-to-tail type was considered using lithium niobate samples with a Z cut and sizes of 20 × 10 × 1 mm with total contents of Fe ions $C_{Fe} \approx 0.05–0.1$ at % and the optimum ratio $Fe^{2+}/Fe^{3+} \sim 0.3$. The complicated laser–acoustic method was used to measure domain sizes and the parameters of photoinduced field E_{ph} [8]. PDSes were formed by irradiating surface Z using laser beams ($\Delta L \sim 30–100$ μm) with a wavelength of 0.53 μm and power densities of up to 10^8 W/m^2. It was first established in [8] that doping congruent samples with Fe ions reduces the initial coercive field; in addition, maximum E_s falls by 25–30% only at optimum ratio $Fe^{2+}/Fe^{3+} \approx 0.25–0.30$. Experiments performed later allowed us to a greater reduction in field E_s due to stronger focusing of a laser beam with an improved uniform mode composition (better by 5–7 kV mm^{-1}).

RESULTS AND DISCUSSION

Analysis of the distribution of gradients of photoinduced fields E_{ph} in the region of irradiation showed that the maximum E_{ph} was located near boundaries of the laser beam closer to negative pole E_s, i.e., asymmetrically to the maximum of the intensity in a laser beam with Gaussian structure. This fully corresponds

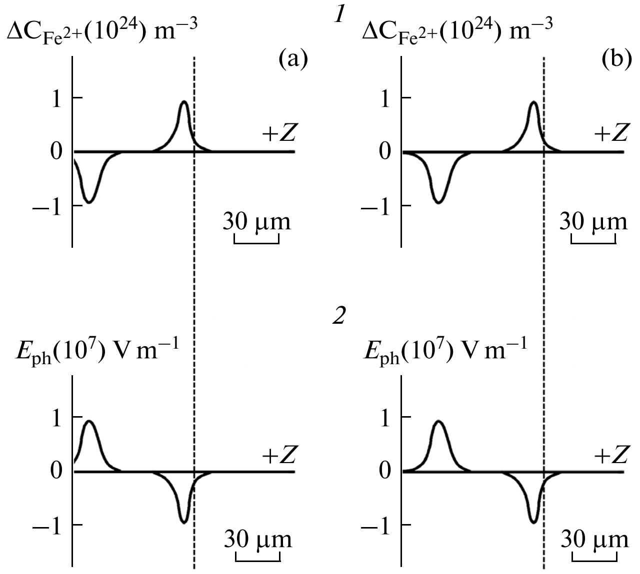

Fig. 1. Structure of the variation in the concentration of (*1*) Fe^{2+} ions $\Delta C_{Fe^{2+}}$ and (*2*) electric field gradients E_{ph} upon the irradiation of (a) the surface of a sample and (b) below the surface.

to the profile of the spatial distributions of Fe^{2+} and Fe^{3+} ions after irradiation (Fig. 1). The width of gradient E_{ph} did not exceed 50–100 μm and depended to some extent on the concentration of Fe ions, the length of irradiation, and the associated diffusion process. The spatial position of the boundaries virtually corresponds to maxima E_{ph} and is also displaced from the center of the beam. This was confirmed experimentally via displacement of a tightly focused beam with a diameter of 30 μm along the Z axis from the surface inside the sample. The formation of a domain near the Z surface was observed when the center of the beam was displaced 50–70 μm from the surface. The domain boundaries were asymmetrical with some smearing of the wall in the zone of irradiation. The steepness of this wall could be raised by applying the laser beam uniformly over the area of the PDS, removing E_{ph} while preserving the domain structure that was formed.

Deformations longitudinal along the Z axis and transverse along axes X and Y, found at the boundaries of the zone of irradiation (Fig. 2), also had the time characteristics of the growth as photoinduced fields, and the values of the relative deformations $\partial U_Z/\partial Z \approx d_{33}E_{ph}(Z)$, where d_{33} is the piezoelectric coefficient ($d_{33} = 0.6 \times 10^{-11}$ C N^{-1}. It is logical to compare the effect of the cooperative ordering of Jahn–Teller Mn^{3+} ions in the manganites studied in [9], which was accompanied by the macrocopic deformation of samples, to the similar deformation of $LiNbO_3$:Fe samples. For lithium niobate, the near doubling of the concentration of Fe^{2+} ions at the boundary of laser irradiation under conditions of easy polarizability leads to macroscopic stretching deformation along the Z axis of polarization. We may therefore assume that in both cases, the dynamics and spatial variations of macrostructural deformations were determined by local deformations of the oxygen octahedra around Jahn–Teller ions induced by magnetic or electric fields, and by the temperature.

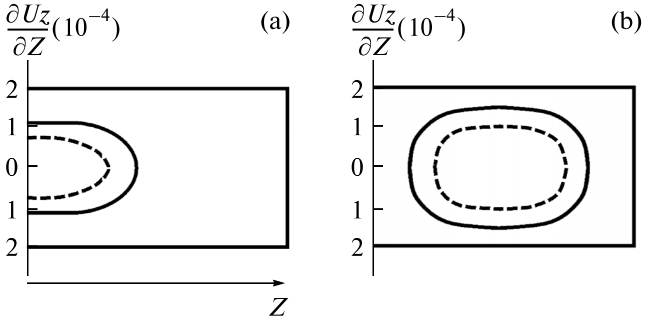

Fig. 2. Photoinduced longitudinal deformations upon the irradiation of (a) the surface of a sample and (b) below the surface (solid lines). The dotted line shows the shape of the laser beam.

CONCLUSIONS

A comparison of our results with existing data shows that

(1) the photoinduced formation of lattices and domains in oxide ferroelectrics is associated with the excitation of electrons from donor centers and their reabsorption by acceptor centers. The result is a considerable reduction in coercive field E_s, particularly in stoichiometric samples of lithium niobate: there is a drop of 2–3.5 kV mm^{-1}, due to the emergence of photoinduced fields (E_{ph});

(2) a much greater reduction in E_s (a drop of 6–7 kV mm^{-1}) is possible only by using the effect of photoionization of doped Jahn–Teller ions (e.g., Fe^{2+} $LiNbO_3$). This effect is associated with the emergence of Jahn–Teller ion oredring and the formation of a charge field (Fe^{2+}–Fe^{3+}) directed opposite E_s;

(3) strong macroscopic elastic deformations in the zone of irradiation appear during the formation of E_{ph} due to local deformations of oxygen octahedra around Jahn–Teller ions.

Our study of the simultaneous impact of an interfering laser beam and a uniform electric field demonstrates the possibility of periodic domain structures forming when a photoinduced field reduces the coercive field in oxide ferroelectrics doped with Jahn–Teller ions.

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