X-ray-induced phase transformation in congruent and vapor-transport-equilibrated lithium tantalate and lithium niobate

V. Ya. Shur,[a] E. B. Blankova, E. L. Rumyantsev, E. V. Nikolaeva, E. I. Shishkin, and A. V. Barannikov
Institute of Physics and Applied Mathematics, Ural State University, Ekaterinburg 620083, Russia

R. K. Route, M. M. Fejer, and R. L. Byer
E. L. Ginzton Laboratory, Stanford University, Stanford, California 94305

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We have discovered an effect of a partially reversible x-ray-induced increase of diffuse x-ray scattering in both congruent and vapor-transport equilibrated single-crystalline lithium niobate and lithium tantalate. The effect has been attributed to x-ray-induced decay of the ferroelectric phase at room temperature. The x-ray-induced change of the switching current and hysteresis loops observed is in accord with this assumption. © *2002 American Institute of Physics.*
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Periodic ferroelectric domain patterning with periods of about several microns (so-called microdomain engineering) has been widely used recently for improving the characteristics of electro-optical and nonlinear optical devices. This new class of periodically poled (PP) nonlinear optical materials is used for the development of tunable coherent light sources based on quasiphase matching.[1,2] Lithium niobate, $LiNbO_3$ (LN), and lithium tantalate, $LiTaO_3$ (LT), are the most important representatives of this class due to their large electro-optical and nonlinear optical coefficients.[3] Domain patterning by application of electric field through lithographically defined electrodes is used for production of such devices.[4,5] However, their extremely high coercive voltage limits the thickness of PP samples. It is crucial to overcome this obstacle for wide usage of PPLN and PPLT devices. The coercive field drastically diminishes with a change in composition from congruent to stoichiometric in both LN and LT.[6] One way to get the lithium content closer to stoichiometry is to use the vapor transport equilibration (VTE) process.[7] It is known that congruent LN (CLN) at low temperatures is metastable. Long-time annealing at a temperature of about 800 °C leads to partial decomposition and the appearance of the second niobium rich nonpolar phase $LiNb_3O_8$.[3] To our knowledge there are no publications about the influence of bulk inclusions of the second phase on the switching characteristics. It is believed that during fast cooling $(dT/dt \sim 100\,^{\circ}\mathrm{C}/h)$ and at room temperature the phase decay is negligible.[3] In this letter we report the discovery of strong x-ray-induced phase decay at room temperature in LN and LT. The effect has been investigated *in situ* by x-ray diffraction. The influence of decay on the switching kinetics is revealed.

Single-crystalline 0.5–0.7-mm-thick plates of congruent LT cut perpendicular to their polar axis were VTE processed[7] by suspending them in a sealed platinum crucible over a two-phase powder of 60 mol % Li_2O and 40 mol % Ta_2O_5. VTE processing was carried out in the temperature range of 1100–1350 °C for periods of 100–200 h. The ambient in the furnace was either atmospheric or slightly oxygen rich. The mixture chosen served as a source of Li_2O with a vapor pressure that corresponds exactly with the vapor pressure of Li_2O over stoichiometric LT at the same temperature.

Co $K\alpha$ radiation was used for the x-ray diffraction study. Two different methods were applied: first, automatic recording of the angular dependence of the x-ray intensity in the θ–2θ regime and, second, recording of the time dependence of the x-ray intensity at fixed angle. The angular sweep rate was 2 deg/min.

The influence of x-ray exposure on the switching characteristics (hysteresis loops and switching currents) was studied in VTE-LT plates with sputtered In_2O_3:Sn transparent electrodes. The switching characteristics were measured before and after x-ray exposure by applying triangular voltage pulses with frequency of 5 Hz. The field amplitude ranged from 2 to 5 kV/cm.

For all samples investigated we recorded weak diffuse scattering over a wide angular range $(15° < 2\theta < 40°)$. The signal was two orders of magnitude less than the narrow intensive peak of the ferroelectric phase [the K_α (006) line of LN or LT]. The angular dependence of the diffuse scattering is smooth for all LN samples [Fig. 1(a)]. In contrast, a fine structure consisting of up to four local maxima occurs in LT samples (both CLT and VTE LT) [Figs. 1(b) and 1(c)]. This

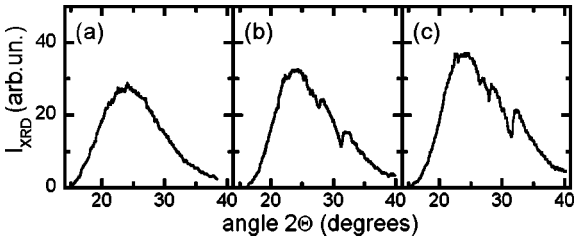

FIG. 1. Angular dependence of the intensity of diffuse x-ray scattering for (a) CLN, (b) CLT, and (c) VTE LT annealed at 1320 °C.

[a]Electronic mail: vladimir.shur@usu.ru

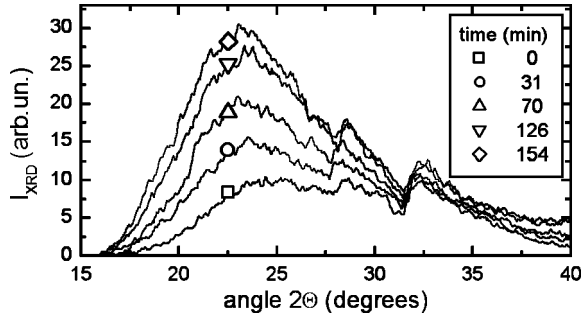

FIG. 2. Diffuse maximum recorded during the set of subsequent measurements with an increase in rest times for VTE LT annealed at 1320 °C.

structure is sensitive to the sample's prehistory and is dependent on the temperature of the VTE process.

An essential change in the angular dependence was revealed for the set of subsequent measurements with increasing rest times (Fig. 2). The time dependence of the diffuse scattering was investigated by recording the intensity at fixed angle in the vicinity of the diffuse scattering maximum (I_{DM}). The three types of I_{DM} time dependence were distinguished.

(1) Fast increase after x-ray switch on. The typical dependence of I_{DM} on x-ray exposure for VTE LN is presented in Fig. 3(a). It is seen that each x-ray switch on leads to a fast increase of I_{DM} with subsequent slow saturation to $I_{\max}$. The growth in intensity was fitted by the following formula for times ranging from 10 s to 250 min:

$$I_{DM}(t) = I_{\max} - \Delta I_f \exp(-t/\tau_f) - \Delta I_s \exp(-t/\tau_s), \quad (1)$$

where ΔI_f and ΔI_s τ_f and τ_s are amplitudes and time constants of fast and slow processes, respectively.

(2) Partial recovery during the rest time (reversible process). The value of $I_{\max}$ remains stable for subsequent exposures, whereas I_{DM} measured at the beginning of each exposure demonstrates an essential decrease compared to $I_{\max}$ (Fig. 3). Thus partial spontaneous recovery occurs during the rest time. The degree of recovery depends on the duration of the rest time (Fig. 3). After a rest time of about 20 h, I_{DM} measured at the beginning of exposure becomes equal to the initial value [cf. Figs. 3(c) and 3(a)].

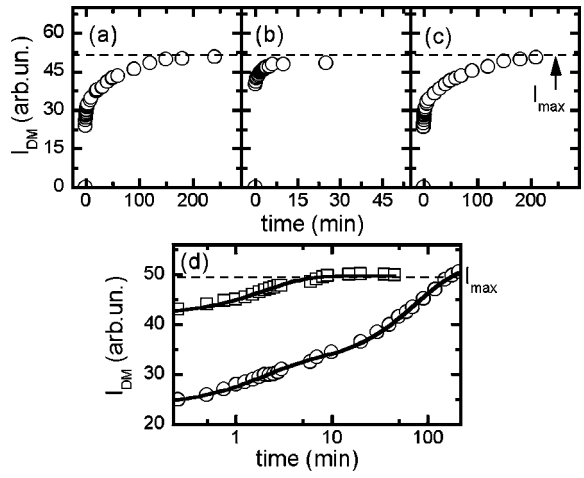

FIG. 3. Dependence of I_{DM} on the x-ray-exposure for VTE LN after different rest times: (a) initial measurement, (b) after 60 min, and (c) after 1100 min. (d) Fitting of (b) and (c) by Eq. (1) ($\tau_f = 2$ min, $\tau_s = 80$ min).

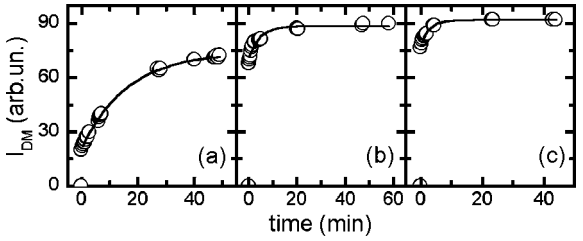

FIG. 4. Dependence of I_{DM} on the x-ray-exposure for VTE LT annealed at 1370 °C after different rest times: (a) initial measurement ($I_{\max}=74$), (b) after 30 min ($I_{\max}=89$), and (c) after 50 min ($I_{\max}=92$). The experimental points are fitted by Eq. (1).

It was found that the ratio of fast and slow amplitudes essentially depends on the duration of the rest time. For a short rest time (up to 60 min) the increase of I_{DM} is governed by the fast process only ($\tau_f \sim 2$ min) (Fig. 3). For rest times of about 20 h the additional input of a slow increase ($\tau_s \sim 80$ min) is essential (Fig. 3).

(3) Increase and decrease of $I_{\max}$ (irreversible process). For many repeated irradiations, the value of $I_{\max}$ becomes dependent on the total time determined as the sum of all of subsequent exposures and rest times. At the beginning of such a long series, $I_{\max}$ increases (Fig. 4). The intensity of diffuse scattering integrated over the whole angle range I_{int} demonstrates similar behavior. It is clearly seen from the series of measurements of the angular dependencies for various rest times in the LT sample for a VTE processing temperature of 1320 °C (VTE LT 1320) (Fig. 5). The observed exponential dependence of I_{int} and I_{DM} on the total time demonstrates that the x-ray-induced transformation continues during the rest time. The time constants obtained are $\tau = 240$ min for I_{int} and $\tau = 150$ min for I_{DM}. These parameters depend on the sample's prehistory and VTE conditions.

For VTE LT 1370, the I_{DM} increase gave way to a slow decrease for a time constant of about 100 min for a long total duration (Fig. 6). An essential decrease of $I_{\max}$ during the rest time is clearly seen at this stage. The angular dependence measured for different total times is presented in Fig. 7.

The typical effect of x-ray exposure on switching characteristics has been studied in VTE LT 1370 (Fig. 8). A significant decrease (about fivefold) of the bias field is observed after 200 min exposure [Figs. 8(a) and 8(b)]. A detailed analysis of the switching current data[8] reveals the qualitative

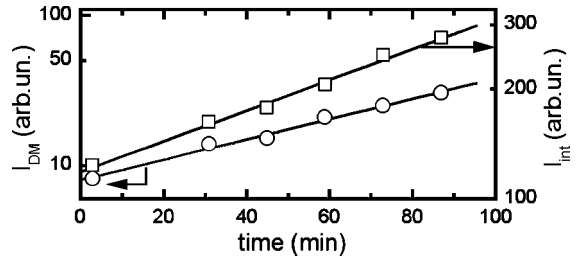

FIG. 5. Dependence of the integral intensity and I_{DM} on the total time for VTE LT annealed at 1320 °C fitted by exponential dependence.

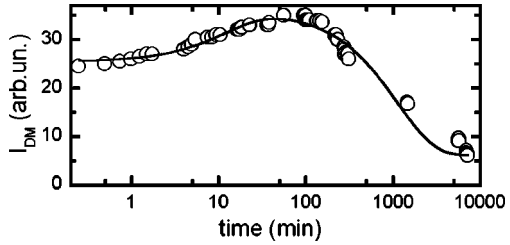

FIG. 6. Dependence of I_{DM} on the total time for VTE LT annealed at 1370 °C. The experimental points are fitted by Eq. (1) ($\tau_f = 13$ min, $\tau_s = 1120$ min).

change of the domain kinetics: a transition from the α to the β process.[8,9] This behavior allows us to suggest that the initial nuclei density (the concentration of residual domains) dramatically increases as a result of exposure [Figs. 8(c) and 8(d)].

The diffuse scattering observed (Fig. 1) is produced by the fine-grained (x-ray amorphous) phase. It is natural to ascribe it in CLN to lithium deficient nonferroelectric $LiNb_3O_8$ phase[3,10] arising as a result of decay of the high-temperature phase, which is metastable at temperatures lower than 910 °C.[3] Thus the resulting increase of the diffuse scattering (Fig. 2) can be attributed to x-ray-induced phase decay at room temperature. The spontaneous decrease of the diffuse scattering during the rest time (Fig. 3) is due to a decrease of the x-ray-induced phase (partial recovery of the initial metastable phase) after termination of exposure.

The displacement phase transition can be considered as the most probable reason, because atom diffusion is negligible at room temperature. Moreover it is known that such transitions demonstrate both reversible and irreversible behavior, e.g., thermoelastic (martensite-type) transformation in copper-, silver-, gold-, and titanium-based alloys.[11–13] In analogy to martensites nuclei growth during x-ray exposure is divided into two stages. At the first ''pre-transition stage'' the coherent boundary between the induced and metastable phases remains. Thus the induced phase becomes unstable after termination of exposure and partial recovery occurs. The crystallite of the induced phase becomes stable when its size overcomes the critical value for which the mutual coherence between metastable and induced phases is destroyed. The growth of x-ray-induced stable crystallites continues during the rest time. The irreversible decrease of the diffuse intensity after multiple exposure (Fig. 6) can be ascribed to

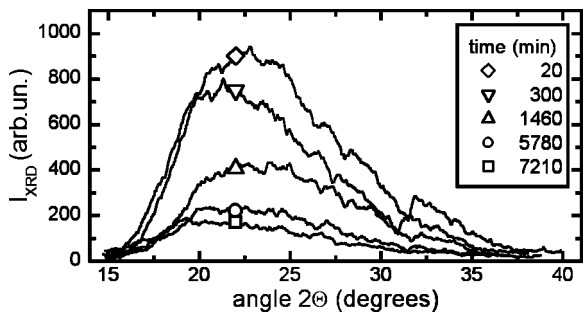

FIG. 7. Diffuse maximum recorded during the set of subsequent measurements for different total times for VTE LT annealed at 1370 °C.

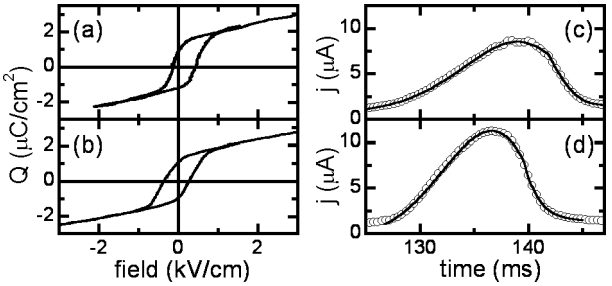

FIG. 8. (a), (b) Hysteresis loops and (c), (d) switching currents for VTE LT annealed at 1370 °C (a), (c) before and (b), (d) after x-ray-exposure for 200 min.

this growth, because the diffuse scattering diminishes with an increase in crystallite size. We propose that x-ray-induced decay occurs in LT as well, because the dependencies for CLT and VTE LT obtained are similar to those discussed above for CLN.

Evolution of the switching current data confirms the proposed approach. The appearance of nonpolar phase regions induced by x rays leads to the appearance of a depolarization field at the interphase boundaries. The residual domains that arise as a result of switching under this field facilitate the switching process thus changing the domain kinetics from α to β process [Figs. 8(c) and 8(d)].[8,9]

We have discovered the effect of an x-ray-induced increase of the intensity of diffuse x-ray scattering in LN and LT single crystals. The effect is attributed to reversible and irreversible x-ray-induced phase transformations at room temperature. The essential irreversible change of the switching properties as a result of x-ray exposure that was revealed can be used for local modification of LN and LT crystals, thus opening up a new area of domain engineering.

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