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, LiNbO₃ (LN), and lithium tantalate, LiTaO₃ (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 LiNb₂O₆.3 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 the influence of bulk inclusions of the second phase on the switching characteristics was negligible.3 In this letter we report the discovery 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.

Periodic ferroelectric domain patterning with periods of about several microns 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. Lithium niobate, LiNbO₃ (LN), and lithium tantalate, LiTaO₃ (LT), are the most important representatives of this class due to their large electro-optical and nonlinear optical coefficients. Domain patterning by application of electric field through lithographically defined electrodes is used for production of such devices. 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. One way to get the lithium content closer to stoichiometry is to use the vapor transport equilibration (VTE) process. 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 LiNb₂O₆. 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 the influence of bulk inclusions of the second phase on the switching characteristics was negligible. In this letter we report the discovery 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.

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.

**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.
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:

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

where $\Delta I_f$ and $\Delta I_s$, $\tau_f$ and $\tau_s$ 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)].

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 reveals the qualitative...
change of the domain kinetics: a transition from the $\alpha$ to the $\beta$ process.\textsuperscript{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$_3$O$_8$ phase\textsuperscript{3,10} arising as a result of decay of the high-temperature phase, which is metastable at temperatures lower than 910 °C.\textsuperscript{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.\textsuperscript{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 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 $\alpha$ to $\beta$ process [Figs. 8(c) and 8(d)].\textsuperscript{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.

The research was made possible in part by the Programs “Basic Research in Russian Universities” under Grant No. 5563 and “Priority Research in High School Electronics,” under Grant No. 03-03-29, by the Russian Foundation for Basic Research, under Grant No. 01-02-17443, by Civilian Research and Development Foundation, under Award No. REC-005, and by the TRW Foundation, CNOM.