Polarization reversal and domain grating in flux-grown KTiOPO$_4$ crystals with variable potassium stoichiometry

G. Rosenman,[a] P. Urenski, and A. Arie
Department of Electrical Engineering-Physical Electronics, Tel Aviv University, Ramat-Aviv 69978, Israel

M. Roth
School of Applied Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

N. Angert and A. Skliar
Raicol Crystals Ltd., P.O.B. 3, Ariel 44837, Israel

M. Tseitlin
Research Institute, College of Judea and Samaria, Ariel 44837, Israel

A significant decrease is observed in the dielectric dispersion, conductivity, coercive and internal fields of KTiOPO$_4$ crystals grown with relatively high potassium concentration in the flux. A periodic domain structure with a period of 24.7 μm was fabricated on a 10 mm long crystal by electric field poling. Whereas standard flux-grown KTiOPO$_4$ crystals can be periodically poled only at low temperatures (near 170 K), the periodic poling in this case was successfully performed near room temperature at a much lower electric field. Quasiphase-matched frequency doubling of 1550 nm radiation was achieved with the poled crystal. © 2000 American Institute of Physics. [S0003-6951(00)00925-6]

The quasiphase-matching technique based on engineered ferroelectric domain configurations is a promising technique for the development of a new generation of coherent light sources.[1,2]

Flux-grown KTiOPO$_4$ (KTP) crystals[3] exhibit a low value of a coercive field $E_C = 25$ kV/cm at room temperature T_R but they are characterized by high conductivity, typically of 10^{-7} Ω^{-1} cm^{-1}. As a result poling performed with a low electric field at T_R produces substantial domain broadening in PP structures of KTP crystals.[4] In the works[5,6] a low temperature poling method of tailoring PP domain configurations in flux-grown KTP family crystals has been proposed. However, temperature lowering causes a strong enhancement of the switching coercive field from $E_C = 25$ kV/cm at $T = T_R$ to $E_C = 120$ kV/cm at $T = 170$ K.[5]

Studies of LiNbO$_3$ and LiTaO$_3$ crystals[7,8] revealed a dramatic reduction of the coercive fields, four- to five-fold in LiNbO$_3$ and 13-fold in LiTaO$_3$ stoichiometric crystals, as compared to their nonstoichiometric compositions. Deviation from stoichiometry is known to exist in flux-grown KTP crystals, and it is mainly attributed to nonstoichiometric defects in the potassium and oxygen sublattices.[9] In this letter we present experimental results on polarization reversal and dielectric spectroscopy of flux grown KTP crystals with different potassium nonstoichiometries.

Specifically for this study, KTP crystals were grown with variable initial concentrations of KTP in the flux.[10] Dielectric spectroscopy and dc conductivity were studied using a computerized data systems based on a Hewlett–Packard model 4284A Precision *LCR* meter (frequency range 100 Hz–1 MHz) and a Hewlett–Packard 4339B high resistance

meter. Silver paint electrodes were deposited on both polar Z faces. The conductivity was measured by a two point method. The spontaneous polarization of the samples and coercive fields were measured from dielectric hysteresis loops using a ferroelectric tester (Radiant Technology Inc.).

Three types of samples were prepared from three different crystals grown with relatively high, intermediate and lower KTP (or potassium) concentrations in the flux. We presume that the crystals also differ in potassium content correspondingly and denote them as HK, IK, and LK, for high, intermediate, and lower K content, respectively. Relative evaluation of the K content in KTP crystals is possible using the ferroelectric–paraelectric transition temperature (the Curie point T_C) measurements.[10] Higher T_C values indicate a higher K content.[11] Although the Curie points of our three KTP samples vary weakly (within 5° around $T_C = 950$ °C), their experimentally measured dc conductivities vary rather strongly. The dc conductivity of the LK sample at T_R is $\sigma = 10^{-8}$ Ω^{-1} cm^{-1}. It exceeds the HK crystal conductivity by 4 orders of magnitude. Measurements of the LK sample conductivity as a function of temperature shows that $\sigma = 10^{-12}$ Ω^{-1} cm^{-1} is achieved at a temperature of about $T \sim 170$ K.

The dielectric permittivity ϵ' measured at $T = T_R$ for the LK crystal shows a high dispersion at low frequency, $\Delta\epsilon' \sim 10^3$ (Fig. 1) and substantial dielectric losses tan $\delta > 1$. These parameters exceed the dielectric dispersion $\Delta\epsilon'$ and tan δ for the HK sample by 2 orders of magnitude. Reduction of temperature from T_R to $T = 170$ K leads to a strong suppression of the dielectric response in the LK sample by almost 2 orders of magnitude, while the dielectric permittivity of the HK crystal composition decreases rather feebly by 10%–15% in a similar temperature range. The dielectric permittivity ϵ' of the LK crystal at $T = 173$ K is close to ϵ' of the

[a]Author to whom correspondence should be addressed; electronic mail: gilr@eng.tau.ac.il
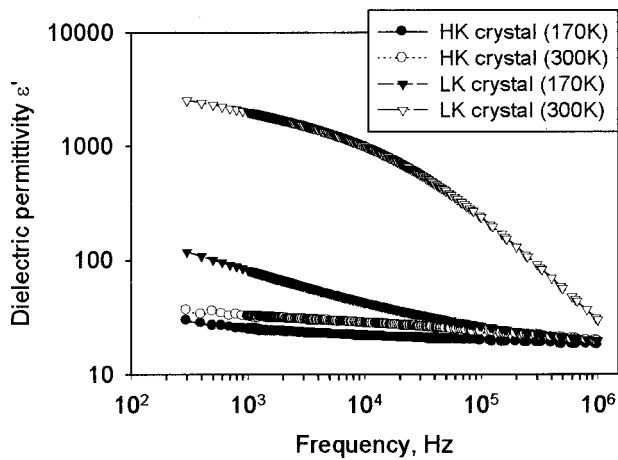
FIG. 1. The dielectric permittivity of KTP crystals with variable potassium (K) stoichiometry.

HK sample measured at room temperature (Fig. 1).

Measurements of the hysteresis loops of the LK crystals at T_R have led to electrical breakdown because of the high conductivity. Therefore, the sample demonstrates the hysteresis loop at a lower temperature of $T = 190$ K [Figs. 2(a) and 2(b)]. The loop is unsaturated, with saturation value of spontaneous polarization $P_S = 57 \, \mu\text{C/cm}^2$ which exceeds almost twice the value of P_S for KTP measured in the work.[3] The coercive field for the LK sample is $E_C = 120$–150 kV/cm, in close similarity to our earlier measurements performed on regular KTP crystals.[5] In contrast, the HK sample exhibits a classic saturated loop already at T_R. The obtained value of $P_S = 27 \, \mu\text{C/cm}^2$ is close to the known for P_S of KTP crystals.[3] The measured coercive field is low, $E_C = 29$ kV/cm, which is about 4–5 times lower than the coercive field of the LK crystal.

Both hysteresis loops, corresponding to HK and IK samples, are asymmetric $E_{+C} > E_{-C}$ (Fig. 2). High conductivity of the LK crystal with low K content allowed us to observe the hysteresis loops at low temperature region only. Measurements of the coercive fields E_{+C} and E_{-C} of the HK- and IK-type samples have been carried out for a wide temperature region, and the results are given in Fig. 3.
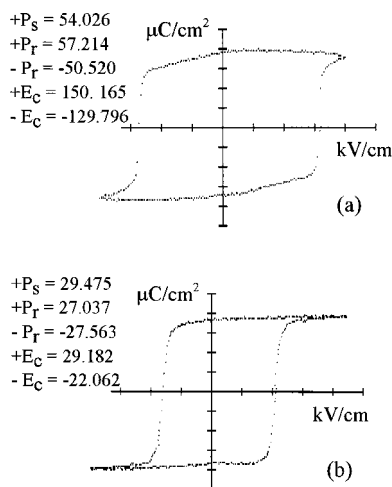

+P_S = 54.026 μC/cm^2
+P_r = 57.214
- P_r = -50.520
+E_C = 150. 165
- E_C = -129.796

kV/cm

(a)

+P_S = 29.475 μC/cm^2
+P_r = 27.037
- P_r = -27.563
+E_C = 29.182
- E_C = -22.062

kV/cm

(b)

FIG. 2. Hysteresis loops for KTP crystals with variable potassium stoichiometry: (a) LK sample measured at $T = 190$ K; (b) HK sample measured at $T = 300$ K.
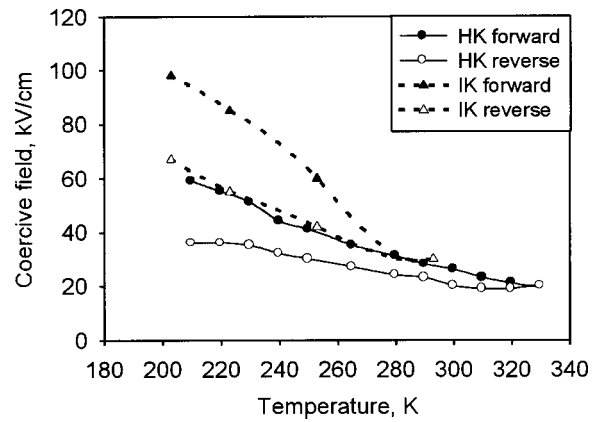

FIG. 3. The temperature dependence of the coercive field for forward E_{+C} and reverse E_{-C} poling for IK and HK KTP samples.

The model of polarization switching proposed by Landauer[12] showed that a minimization of the depolarization energy U_d plays a crucial role in the polarization switching process. The general equation for the screening charge may be written as follows:

$$Q_\Sigma = \int_0^{\tau_{sw}} J_{ext} + Q_{b0}[1 - \exp(-t/\tau)], \qquad (1)$$

where τ is the dielectric relaxation time. The first term is a conventional switching charge Q_{ext} brought by the transient switching current J_{ext} to switching electrodes via the external circuit during switching time τ_{sw}. The second screening charge Q_b, is provided by the bulk conductive current J_b. This occurs due to a relaxation process via bulk crystal conductivity. The relaxation time τ is defined as $\tau = \epsilon \epsilon_0 / \sigma$. A ferroelectric crystal is commonly described as an ideal dielectric and the contribution of the second term in Eq. (1) is negligibly small. During polarization switching, a displacement switching current occurs in a ferroelectric crystal bulk while a transient switching current J_{sw} [the first term in Eq. (1)] flows in the external short circuit.

Regular flux grown KTP LK crystals, which are similar to our LK samples exhibit $\Delta \epsilon' \sim 10^3$, $\tan \delta > 1$ and dc conductivity $\sigma = 10^{-8} \, \Omega^{-1} \, \text{cm}^{-1}$ (Fig. 1). Such properties give direct evidence for a highly pronounced relaxation process in the KTP crystal lattice. The existence of a relatively "mobile" K sublattice explains the one-dimensional ionic conductivity in KTP crystals,[13] which is thought to be related to the movement of K$^+$ ions through K vacancies V'_K along the channels. The vacancies are created due to a loss of O$_2$ accompanied by a loss of K (for charge compensation) at elevated growth temperatures. Thus intrinsic defects, such as singly ionized K vacancies and doubly ionized oxygen vacancies ($V_O^{\bullet\bullet}$) are formed at the growth temperature

$$O \rightarrow 2V'_K + V_O^{\bullet\bullet}, \qquad (2)$$

where V'_K and $V_O^{\bullet\bullet}$ are intrinsic onefold negatively charged potassium and twofold positively charged oxygen vacancies formed at temperature growth. The concentration of V'_K reaches 1% at T_R and provides high mobility of the K$^+$ ions with activation energy $E_a = 0.3$ eV.[14] Investigation of defects in KTP crystals[9] showed no significant nonstiochiometry of the TiO$_2$ and phosphate sublattices. The influence of K$^+$

ionic conductivity is clearly observed during polarization switching. The K$^+$ ionic current contributes significantly to the measured switching charge P in the LK sample (with lower K content) via the second term Q_b of Eq. (1) [see also Fig. 2(a)]. Lowering temperature leads to a decrease in the K$^+$ hopping conductivity which is manifested in the reduction of the dielectric dispersion and the dissipation factor (Fig. 1).

In IK and NK crystals, namely of higher K content, substantial changes in the relaxation processes, charge transport and polarization switching are revealed. Weak $\Delta\epsilon'$ (Fig. 1), low dissipation factor $\tan\delta\sim10^{-2}$, dc conductivity reduction in 4 orders of magnitude (to $\sigma=10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) and the observed saturated hysteresis loop at T_R, is characteristic for HK-type crystals containing fewer potassium vacancies.

The potassium vacancies represent charged point defects. They may interact by means of pinning and depinning the movement of the domain walls during polarization switching. The effect of the charged vacancies on the coercive field is unusually strong in nonstoichiometric LiNbO$_3$ and LiTaO$_3$ crystals.[7,8] Our measurements on KTP crystals (Figs. 2 and 3) show that the bias internal field E_{in} is determined by the K deviation from stoichiometric composition and depends on temperature. The field E_{in} is $E_{in}=0.5(E_{+C}-E_{-C})$. The asymmetry of the hysteresis loops and field E_{in} disappears at $T=T_0$, while $T_0=330$ K for the HK crystal and $T_0=290$ K for the IK crystal (Fig. 3). One can assume that the built-in field E_{in} formed by K vacancies is screened by K$^+$ ions that are mobile at this temperature. The compensation of the negatively charged K vacancies may be considered as a redistribution of mobile positive potassium space charge across the vacant sites during polarization switching time $t=\tau_{\mathrm{sw}}$. The process is determined by the relaxation time τ. The charge Q_0 of the K vacancies is screened in accordance with the following equation:

$$Q = Q_0 \exp\left(-\frac{t}{\tau}\right). \tag{3}$$

The dielectric hysteresis loops (Fig. 2) were measured with pulse duration 0.5 s which gives $\tau_{\mathrm{sw}}=0.25$ s. The measured ϵ' and σ for IK and HK samples show identical values of $\tau\sim0.18$ s for the respective temperatures $T_0=290$ K (IK sample) and $T_0=330$ K (HK sample). Equation (3) indicates that for $\tau\sim\tau_{\mathrm{sw}}$ the built-in ''vacancy'' field E_{in} will be compensated, which is observed at the point $E_{+C}=E_{-C}$ (Fig. 3). The value of E_{in} is a function of temperature and it is considerably larger for the IK sample than for the HK sample for the temperatures lower T_0. The actual values are $E_{in}=15$ kV/cm at 210 K for the IK sample and $E_{in}=6$ kV/cm at 250 K for the HK sample. Our results for the HK and IK-type KTP crystals are consistent with the proposed model[7,8] where the higher concentration of vacancies causes an increase in the E_{in} field.

A PP domain structure for frequency doubling of $\lambda=1.55$ μm (grating period 24.7 μm) was fabricated in the IK KTP crystal of 10 mm length and 0.5 mm thickness at $T=-25\,°$C where its conductivity decreases to the value $\sigma\sim10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ in accordance with the developed
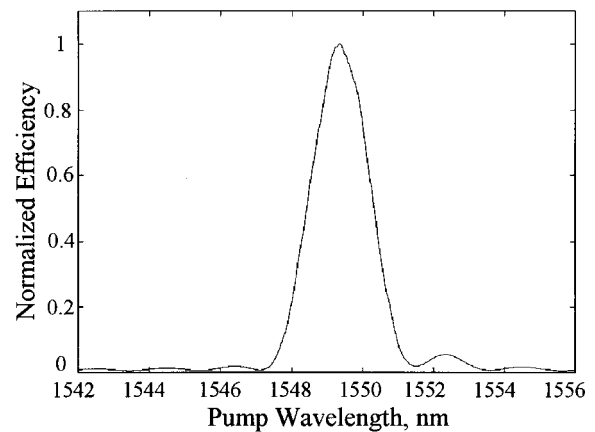

FIG. 4. Second harmonic power as a function of the fundamental power for intermediate K content (IK) PP KTP crystal.

method.[5] The applied field was 46 kV/cm which is in 3.5 times less than the poling field used for PP–KTP fabrication with low K content.[5] The obtained PP configuration possessed 50% duty cycle without any domain broadening. A tunable external cavity diode laser (New Focus, model 6328-H) was used as the pump source. Figure 4 shows the second harmonic power as a function of the fundamental power. The highest doubling efficiency is obtained at 1549.5 nm, which is in excellent agreement with the recently published dispersion equation[15] of KTiOPO$_4$. The wavelength bandwidth (full width at half maximum ≈1.85 nm) corresponds to an effective doubling length of 9 mm, which is in good agreement with the 10 mm physical length of the device. At an input fundamental power of 18 mW, the measured second harmonic power is 330 nW. The effective nonlinear coefficient is ≈6.9 pm/V.

[1] L. M. Myers, R. C. Eckardt, M. M. Fejer, and R. L. Byer, J. Opt. Soc. Am. B **12**, 2102 (1995).

[2] G. Rosenman, A. Arie, and A. Skliar, Ferroelectrics Rev. **1**, 4 (1999).

[3] G. Rosenman, A. Skliar, M. Oron, and M. Katz, J. Phys. D: Appl. Phys. **30**, 277 (1997).

[4] G. Rosenman, A. Skliar, D. Eger, M. Oron, and M. Katz, Appl. Phys. Lett. **73**, 865 (1998).

[5] G. Rosenman, A. Skliar, D. Eger, M. Oron, and M. Katz, Appl. Phys. Lett. **73**, 3650 (1998).

[6] G. Rosenman, A. Skliar, Y. Findling, P. Urenski, A. Englander, P. Thomas, and Z. Zhu, J. Phys. D: Appl. Phys. **32**, L49 (1999).

[7] V. Gopalan, T. E. Mitchell, Y. Furukawa, and K. Kitamara, Appl. Phys. Lett. **72**, 1981 (1998).

[8] K. Kitamara, Y. Furukawa, K. Niwa, V. Gopalan, and T. E. Mitchell, Appl. Phys. Lett. **73**, 3079 (1998).

[9] P. A. Morris, A. Ferreti, J. D. Bierlein, and G. Loiaconno, J. Cryst. Growth **109**, 367 (1990).

[10] N. Angert, M. Tseitlin, E. Yashchin, and M. Roth, Appl. Phys. Lett. **67**, 1941 (1995).

[11] M. Roth, N. Angert, M. Tseitlin, and A. Alexandrovski (unpublished).

[12] R. Landauer, J. Appl. Phys. **28**, 227 (1957).

[13] L. K. Cheng and J. D. Bierlein, Ferroelectrics **142**, 209 (1993).

[14] S. Furusawa, H. Hayasi, Y. Ishibashi, A. Miyamoto, and T. Sasaki, J. Phys. Soc. Jpn. **62**, 183 (1993).

[15] K. Fradkin, A. Arie, A. Skliar, and G. Rosenman, Appl. Phys. Lett. **74**, 914 (1999).