Retardation of Polarization in Mixed $K_{0.88}(NH_4)_{0.12}H_2PO_4$ Crystal

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Abstract—The time dependences of polarization of $K_{0.88}(NH_4)_{0.12}H_2PO_4$ mixed crystal have been studied within the temperature range of 74–100 K. Two mechanisms of polarization relaxation were found. The first mechanism is caused by domain walls lateral motion and their interaction with point lattice defects. The second one supposedly is due to polar regions infiltration through the regions of frustrated paraelectric phase.

INTRODUCTION

$K_{1-x}(NH_4)_xH_2PO_4$ mixed crystals are well known as objects in which dipole glass state characterized by random proton ordering in O–H...O hydrogen bond network is realized at specific ingredient ratios ($0.20 \leq x \leq 0.70$) and in low temperatures. Crystals with ammonium concentration of $x \leq 0.2$ undergo a transition to the ferroelectric phase [1–3] that results in a crystalline structure similar to that of nominally pure potassium dihydrogen phosphate [4, 5].

Partial substitution of potassium ions by NH_4 groups leads to a lowering of the ferroelectric phase transition (T_C) temperature and its noticeable blurring. This is associated with the fact that the ammonium protons, interacting with the nearest oxygen atoms prevent the formation of oxygen–proton configurations corresponding to the ferroelectric (FE) phase, and cause the appearance of local lattice distortions developing in the crystallographic plane ab [4, 5]. Lattice distortions become noticeable in X–ray diffraction experiments below ~100 K and reach maximum in the vicinity of T_C [6]. In the ferroelectric phase, they gradually decrease with cooling of the sample. The transition to the polar phase with decreasing temperature in FE crystals with a high concentration of ammonium is this realized via an intermediate heterophase condition characterized by the coexistence of randomly deformed zones of paraelectric and polar phases. Random local lattice distortions are a source of random fields, a description of which requires the introduction of the Edwards–Anderson parameter q_{EA}. Moreover, as the analysis of NQR [75]As spectra of $Rb_{1-x}(ND_4)_xH_2AsO_4$ mixed crystals [7], the appearance of parameter q_{EA} higher than T_C is observed even at low ammonium concentrations (1 – 2%).

The main aim of this work is to study the effect of the system microheterogeneity on the polarization retardation process in monocrystalline $K_{0.88}(NH_4)_{0.12}H_2PO_4$ undergoing FE phase transition at $T_C \approx 81$ K [2].

EXPERIMENTAL

A sample in the form of a ~6 × 7 × 0.7 mm plate cut from the transparent part of a$K_{0.88}(NH_4)_{0.12}H_2PO_4$ monocrystal was prepared for the experiment. Electrodes on the sample surfaces perpendicular to the tetragonal axis c were created by thermal dispersion of silver in vacuum.

The sample was placed in the cryostat where temperature was varied from 70 to 300 K with an accuracy of no less than ±0.1 K. To obtain the polarization time dependence (P), the sample was cooled from temperature T_A ($T_A \gg T_C$) to the desired temperature in the absence of a measuring field, and the constant field $E = 15$ V/cm was turned on, and the polarization was measured in temperature stabilization mode. This field must be considered weak because it was much lower than the coercive field in the interval of 0.3–1.2 kW/cm in the investigated temperature range [8].

Dielectric constant temperature dependence was measured at 1 kHz in order to clarify the Curie temperature.

The obtained polarization time dependences are shown in Fig. 1. Power, logarithmic, and exponential functions were tested for their analytical description. The best agreement between experimental data with an approximating function was achieved by using the following relationship:

$$P(t) - P_\infty = P_{01}\left\{1 - \exp\left[-(t/\tau_1)^{\gamma 1}\right]\right\} + P_{02}\left\{1 - \exp\left[-(t/\tau_2)^{\gamma 2}\right]\right\}, \quad (1)$$

where P_{01} and P_{02} are values having the sense of polarization saturation processes, described by first and second summands, respectively; P_∞ is the rapidly chang-
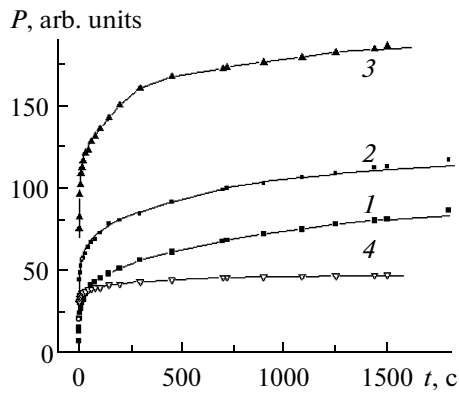
Fig. 1. Polarization time dependences at different temperatures: (*1*) 70; (*2*) 75.5; (*3*) 78.5; (*4*) 80.2 K. Solid lines show the approximating dependences obtained using formula (1).
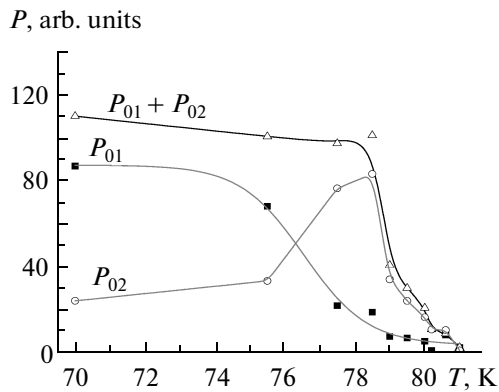

Fig. 2. Parameters P_{01} and P_{02} temperature dependences, and the overall polarization $P_{01} + P_{02}$.
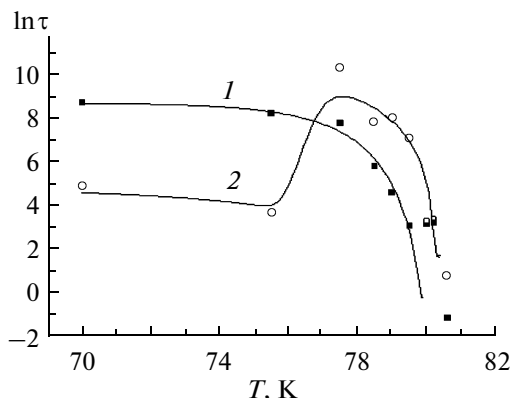

Fig. 3. Temperature dependences of times (*1*) τ_1 and (*2*) τ_2.

ing polarization component; τ_1 and τ_2 are average retardation times; γ_1 and γ_2 are parameters characterizing time distribution τ in respect of its average value ($0 \le \gamma \le 1$). The dependences obtained using expressions (1) are plotted by solid lines in Fig. 1.

The parameters P_{01}, P_{02}, τ_1, τ_2, γ_1, and γ_2, which yield the best experimental data approximation, are presented in Fig. 2 − 4 in the form of respective temperature dependences.

Curve $P_{01}(T)$ decreases with increasing temperature, approaching zero near $T_C \approx 81$ K (Fig. 2). The corresponding retardation time (Fig. 3) falls rapidly as it approaches T_C. The parameter $\gamma_1 \approx 1$, indicating that the value dispersion is quite unimportant.

Analysis of the dependences shows that the retardation process is thermoactive and can be described qualitatively by the model that includes interaction of domain boundaries with mobile point defects. The model yields the following expression for the relaxation time (retardation) [9]:

$$\tau_1 = \frac{kTP_s\varphi}{\alpha q D_0}\exp\frac{U}{kT}. \qquad (2)$$

Here P_s is spontaneous polarization; q is charge of point defect interacting with a domain wall; D_0 is a parameter numerically equal to the diffusion coefficient of the defect at $T \to \infty$, n is the number of domain walls inclined to the twinning plane by angle φ per unit of volume; α is the domain wall with defect electrostatic interaction coefficient; U is the diffusion activation energy of defects.

The spontaneous polarization declines rapidly near T_C. According to (2), it leads to a reduction in time τ_1, provided that the electrostatic interaction coefficient α changes alongside with temperature more slowly than P_s does. Considerably lower than T_C, temperature dependence $P_s(T)$ becomes so weak [8] that we may assume $P_s \approx$ const. Estimates made for these temperatures yield $U \approx 0.055$ eV, which is close to the degree of domain walls with point defects interaction energy in KH_2PO_4 crystal [10]. We may thus assume that the polarization component described by the first summand in (1) is associated with lateral movement of domain walls.

The curves $P_{02}(T)$, $\tau_2(T)$, and $\gamma_2(T)$ are markedly different from the temperature dependences of the respective parameters discussed above (Fig. 2–4). Curves $P_{02}(T)$ and $\tau_2(T)$ pass through maxima around 79 K, which is about 2 K below T_C. At the same time, temperature dependence of the total polarization $P_{01} + P_{02}$ (Fig. 2) is analogous to the $P_s(T)$ dependence in given crystal [9].

Parameter $\gamma_2 \approx 0.3$ at 70 K monotonically falls to zero as we approach the Curie temperature. This shows that the process described by second summand in (1) is characterized by a broad distribution of retardation times, which expand when approaching the phase transition temperature.
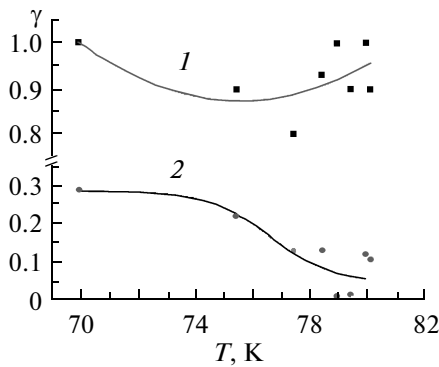
Fig. 4. Temperature dependences of parameters (*1*) γ_1 and (*2*) γ_2.
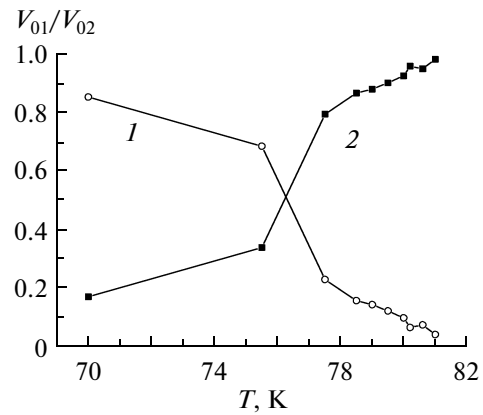

Fig. 5. Temperature dependences of volumes (*1*) V_{01} and (*2*) V_{02}.

Since the P_{02} polarization component is different from zero only in the FE phase, we conclude that it, as well as P_{01}, is associated with the motion of domain walls.

Thus, the experiment shows the presence of at least two forms of domain wall motion which will be called type 1 and type 2 mechanisms, respectively.

Let us discuss the polarization time dependences in the context of the Kolmogorov–Avrami phenomenological theory of phase transitions [11], adapted to describe the repolarization kinetics for ferroelectrics [12].

According to [12], the change in polarization with time is given by $P(t) = 2P_sV(t)$, where P_s is spontaneous polarization, and V is volume fraction of repolarized material. The multiplier 2 appears because the contribution to the polarization change is associated with a decrease in negative domains volume, and with a corresponding increase in the volume of the opposite sign domains.

Based on [11, 12], we can write the expression for the relative increment of the positive domains volume $[\Delta V^+ = V^+(t) - V^+(t=0)]$, polarization vector of which coincides with the applied field:

$$\Delta V^+ = \left\{1 - V_{01}\exp\left[-(t/q_1)^{d1}\right] + V_{02}\exp\left[-(t/q_2)^{d2}\right]\right\}. (3)$$

Here V_{01} is the volume fraction of the crystal that polarizes by a type 1 mechanism; V_{02} is the fraction that polarizes by a type 2 mechanism ($V_{01} + V_{02} = 1$); q_1 and q_2 are kinetic coefficients; and $d1$ and $d2$ are parameters that depend on the growing area dimension D. If the polarization process is not accompanied by the formation of new nuclei, then $d = D$, and in the case of continuous nucleation, $d = D + 1$.

It is easy to see that expressions (3) and (1) are similar, and

$$\Delta V^+ = \frac{P(t) - P_\infty}{P_{01} + P_{02}}, \quad V_{01} = \frac{P_{01}}{P_{01} + P_{02}}, \quad V_{02} = \frac{P_{02}}{P_{01} + P_{02}},$$
$$q_1 = \tau_1, \quad q_2 = \tau_2, \quad d1 = \gamma_1 \quad \text{и} \quad d2 = \gamma_2.$$

It should be noted that the parameter $d1 = \gamma_1 \approx 1$ in the first summand in (3) and, according to Kolmogorov and Avrami [11], corresponds to the one-dimensional motion of the phase boundary without nucleation ($D = 1$). Such motion corresponds to the idea of a lateral regular domain walls movement in the electric field. In the investigated crystal, this mechanism dominates in the temperature range of ≈ 3 degrees below the Curie temperature (Fig. 5).

Near T_C, the most of the positive domain volume increase is due to the second type of mechanism (Fig. 5). The corresponding parameter $d2 = \gamma_2 \ll 1$, which within the Kolmogorov–Avrami formalism corresponds to the fractional space dimension of the polarized area motion ($D \ll 1$). We may assume that an increase in the positively polarized phase volume takes place as it travels through the system of defects formed by random deformations of the lattice, the maximum of which is observed in the vicinity of T_C, according to X-ray [6] and NQR [7] studies on related crystals. This can apparently explain a nonmonotonic temperature dependence τ_2, the maximum of which is located near T_C.

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