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On a low-frequency relaxation in (K, Li)TaO₃ crystals: an influence of the bias field

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Abstract

The low-frequency or π dielectric relaxation in (K, Li)TaO₃ crystals is considered. An analysis of available experimental data on the influence of the bias field on the relaxation frequency enabled a value of the dipole moment of flipping polar elements to be determined for the first time. It is affirmed that they are most probably pairs of rigidly coupled dipoles (dimers) created by off-centre Li ions. The asymmetry changing the Arrhenius law for the mean relaxation time is emphasized and discussed. The dimer concentration and the dimer contribution to the dielectric permittivity are estimated.

1. Introduction

As is well known, two ranges of dielectric relaxation distinguished by the height U of the potential barrier are characteristic of (K_{1-x}Li_x)TaO₃ (KLT) crystals [1–3], i.e. high-frequency or $\pi/2$ relaxation with $U \approx 1000$ – 1200 K and low-frequency or π relaxation with $U \approx 2400$ – 2700 K. The high-frequency relaxation involves 90° reorientations of single dipoles, created by off-centre Li ions, between six equivalent wells on orthogonal axes. This relaxation is observed for any Li-ion concentration x , and has been explicitly studied by authors of numerous publications [2, 4–7]. There is far less information currently available on the low-frequency relaxation, which is usually connected with 180° reorientation of a pair of rigidly bound dipoles (a dimer) [1–3, 6] and is observed only in KLT crystals with large Li-ion concentrations ($x > 0.022$) as additional relaxation maxima in the temperature and frequency curves for the real and imaginary parts of the complex dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$.

In particular, there is not enough information on the influence of the bias electric field E_{\parallel} on the low-frequency relaxation in KLT crystals. Meanwhile, features of the behaviour under a bias field can give relevant data on both the physical mechanism of the relaxation and the nature of the phases arising at various temperatures. In this paper we suggest a mathematical description of the influence of the bias field on mean time and mean frequency of the low-frequency relaxation and discuss the possible mechanism responsible for the low-frequency relaxation mode. It is shown that the reorientation of dimers, created by the off-centre Li ions, is a catalyst for the low-frequency relaxation processes. Our interpretation differs somewhat from that recently proposed in [8] and agrees with a dimer model [1–3, 6].

Table 1. Calculated values of U_0/T and U_0 for the KLT crystals with $x = 0.1$ ($T = 105$ K).

E_{\parallel} (kV cm ⁻¹)	0	1	2
ω_r (10 ⁴ rad s ⁻¹)	1.59	1.90	3.03
U_0/T	0	0.60	1.26
U_0 (K)	0	63	132.5

2. The low-frequency relaxation with the bias field

In KLT crystals the replacement of K ions by small-radius Li ions results in six local minima of a Li potential arising, displaced in [100] directions from centrosymmetric positions in the paraelectric phase. At the zero bias field, all Li-ion local minima have equal depth, which is defined with respect to the potential barrier height U , and identical displacements $\delta = (0.5\text{--}0.7)$ Å [7, 9, 10] from the centrosymmetric positions. Occupying these positions, Li ions are characterized by electric dipole moments $\mu = se\delta = (0.3\text{--}0.4) e$ Å where e and $s \approx 0.55$ [11] are the elementary charge and ionicity, respectively.

Switching on E_{\parallel} in one of the [100] directions results in asymmetrical distortion of the potential relief for a flipping polar element (a single Li ion or cluster). Such distortion can be characterized by the value U_0 of the half-difference of the base levels of two potential minima arranged in an E_{\parallel} -direction. As a result, there is a change in the mean relaxation time:

$$\tau = \tau_0 \exp(U/T) / \cosh(U_0/T) \quad (1)$$

which decreases as $\cosh(U_0/T)$ increases [12]. This results in increasing a circular frequency of the relaxation of $\omega_r = 1/\tau$. The last effect for $(\text{K}_{0.9}\text{Li}_{0.1})\text{TaO}_3$ was clearly established in [3]: a displacement of the frequency ω_r of the $\varepsilon''(\omega)$ maximum, ε''_m , at the temperature $T = 105$ K. According to the data from [3], $\tau = 0.63 \times 10^{-4}$ s at $E_{\parallel} = 0$ whereas $\tau = 0.33 \times 10^{-4}$ s at $E_{\parallel} = 2$ kV cm⁻¹, i.e. the relaxation frequency ω_r almost doubles, from 1.59×10^4 rad s⁻¹ up to 3.03×10^4 rad s⁻¹.

The values of U_0/T and U_0 calculated by using equation (1) in combination with $\varepsilon''(\omega, E_{\parallel})$, $U = 2388$ K and $\tau_0 = 8.26 \times 10^{-15}$ s from [3] are listed in table 1. As seen from table 1, U_0 can be considered to be proportional to E_{\parallel} , i.e. $U_0 = \mu_0 E^*$ where μ_0 is the electric dipole moment of the flipping polar element (cluster) located in an effective field $E^* \propto E_{\parallel}$ accountable for the asymmetry of the potential relief. The ratio of E^* to E_{\parallel} depends on the dielectric permittivity $\varepsilon_r = (\varepsilon^{\text{LF}} + \varepsilon^{\text{HF}})/2$ at the frequency $\omega = \omega_r$, where ε^{LF} and ε^{HF} are the static (measured at frequencies $\omega \ll \omega_r$ and incorporating a relaxation contribution) and high-frequency (measured at frequencies $\omega \gg \omega_r$ where there is no relaxation contribution) permittivities, respectively. The value $(\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}})$ can be evaluated by using the Cole–Cole formula for $E_{\parallel} = 0$:

$$\varepsilon''_m = [(\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}})/2] \cos(\pi\alpha/2) / (1 + \sin(\pi\alpha/2)) \quad (2)$$

as well as ε''_m - and α -data from [3]. This yields $(\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}}) = 1800$, which is in very good agreement with our earlier estimates $\varepsilon^{\text{LF}} \approx 3300$ and $\varepsilon^{\text{HF}} \approx 1500$ for $(\text{K}_{0.9}\text{Li}_{0.1})\text{TaO}_3$ crystals [13]. Thus, we have $\varepsilon_r \approx 2400$. The results of our calculations of the effective cluster dipole moments μ_0 for different values of the effective field E^* are shown in table 2.

3. Results and discussion

As follows from table 2, the effective cluster dipole moment μ_0 can be interpreted as the dimer moment $\mu_{\text{dim}} \approx 2\mu$ only if the effective field E^* on the cluster equals the Lorentz field

Table 2. Calculated cluster dipole moments for the KLT crystals with $x = 0.1$ ($U_0 = 132.5$ K, $\varepsilon_r = 2400$, $T = 105$ K).

E^*	$2E_L$	E_L	$0.2E_L$	$0.1E_L$	E
μ_0 ($e \text{ \AA}$)	0.357	0.714	3.57	7.14	571

$E_L = (\varepsilon_r + 2)E_{\parallel}/3$. This possibility is expected to be the most probable, as the effective field on the dimer, flipping as rigid whole, should be calculated disregarding interactions of intrinsic dimer atoms. This effective field should be close to the Lorentz field. Earlier, we used the Lorentz field for the analysis of the low-frequency relaxation in KLT crystals [13]. The remaining cases listed in table 2 cannot be explained from the physical point of view. A situation with $E^* = E_{\parallel}$ seems to be completely improbable, as the size of the corresponding cluster is much greater than the correlation length $\sim 40 \text{ \AA}$ [14]. The cases of $E^* = (0.1-0.2)E_L$ correspond to an effective field on Li ions [7] and should also be discarded, as the corresponding electrical dipole moments μ_0 are several times greater than the moment μ created by single off-centre Li ion.

The case with $E^* = 2E_L$ and $\mu_0 \approx \mu$ is worthy of particular notice. In this case, flipping dipoles, which are created by individual off-centre Li ions, are responsible for the low-frequency relaxation. According to [8], just such a single-ion relaxation prevails in the experimental data from dielectric spectroscopy. In our opinion, such an assumption is in error. The problem is not so much the impossibility of explaining the value $E^* \approx 2E_L$ for the effective field on the cluster as the huge difference between the times τ^{LF} of the low-frequency relaxation and τ^{HF} of the high-frequency relaxation. It should be noted that the τ^{LF} -value is six orders of magnitude greater than the τ^{HF} -value [2]. Consequently, thermodynamic equilibrium, after switching on or changing the electric field, will be restored only by using the $\pi/2$ relaxation mode. There will not be non-equilibrium Li ions available for implementation of the slow π processes—whose probability of realization is $\sim 10^6$ times less than that for the $\pi/2$ ones.

Thus, the electric dipole moment of the cluster, which is responsible for the displacement in the bias field of the relaxation frequency $\omega_r = 1/\tau$ of the low-frequency relaxation, is close to the moment of the dimer. In [3], the asymmetry of the potential relief arising under the bias electric field is also noted, but there is no analytical description, such as that given by our formula (1). Moreover, it is considered that it is not asymmetry of the relief but an increase of the degree of ordering that is responsible for the decrease in the relaxation time.

In order to determine the number of the dimers in unit volume and their contribution to the relaxation dielectric permittivity ($\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}}$), we have to take into account that the main contribution to ε' for KLT crystals stems from Ta and O₁ ions. Due to the interaction between phonon and relaxation modes, a dimer relaxation appears which results in the change of the effective fields on the Ta and O₁ ions that, in turn, is the cause for the contribution of these ions to $\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}}$ [7]. Using data from our previous calculations [7], we can easily estimate the contribution of the Ta and O₁ ions to ε^{HF} and a corresponding polarization P^{HF} :

$$P^{\text{HF}} = \varepsilon_0(\varepsilon^{\text{HF}} - 1)E \approx N_0(5.1\alpha_2 + 3.8\alpha_3)\varepsilon_0(\varepsilon^{\text{HF}} + 2)E/3 \quad (3)$$

where α_2 and α_3 are total polarizabilities of the Ta and O₁ ions. By using factors of 5.1 and 3.8, we take into account the difference between the Lorentz field $(\varepsilon^{\text{HF}} + 2)E/3$ and the effective fields E_2^* and E_3^* on the Ta and O₁ ions; $N_0 = 1/v^3$, v is the unit-cell volume and ε_0 is the dielectric permittivity of free space. Thus, because $\varepsilon^{\text{LF}} \gg 1$, $\varepsilon^{\text{HF}} \gg 1$, we obtain

$$N_0(5.1\alpha_2 + 3.8\alpha_3)/3 \approx 1. \quad (4)$$

The appearance of the dimer relaxation polarization leads to practically the same changes in E_2^* and E_3^* by the factor b ($1 - |b| < 0.1$ [7]). This factor does not depend on the Li-ion

concentration x and the corresponding contribution to ε^{LF} , and the low-frequency polarization P^{LF} is expressed by the formula

$$P^{\text{LF}} = \varepsilon_0(\varepsilon^{\text{LF}} - 1)E \approx [N_0b(5.1\alpha_2 + 3.8\alpha_3) + N_{\text{dim}}\mu_{\text{dim}}^2/(3T)]\varepsilon_0(\varepsilon^{\text{LF}} + 2)E/3. \quad (5)$$

Hence, $N_0[b(5.1\alpha_2 + 3.8\alpha_3) + (N_{\text{dim}}/N_0)\mu_{\text{dim}}^2/(3T)]/3 \approx 1$ and

$$[N_{\text{dim}}\mu_{\text{dim}}^2/(9T)] \approx 1 - b. \quad (6)$$

For $\mu_{\text{dim}} \approx 2\mu \approx 0.7 e \text{ \AA}$ and $T = 105 \text{ K}$ [3] we obtain $N_{\text{dim}}/N_0 < 5 \times 10^{-3}$ or $N_{\text{dim}}/N_{\text{Li}} < 5 \times 10^{-2}$. Thus, the dimer concentration N_{dim} and the dimer contribution to the ε' -value, $\Delta\varepsilon_{\text{dim}} \approx N_{\text{dim}}\mu_{\text{dim}}^2(\varepsilon^{\text{LF}} + 2)/(9T) \approx 100\text{--}200$, are substantially less than N_{Li} and the total contribution to the relaxation dielectric permittivity ($\varepsilon^{\text{LF}} - \varepsilon^{\text{HF}}$) ≈ 2000 , respectively. Hence, the reorientation of dimers, created by the off-centre Li ions, is a catalyst for the low-frequency relaxation processes.

In summary, it is necessary to stress that the bias-field shift is observed not only for ω_r at $T = \text{constant}$, but also for the relaxation temperature T_r at $\omega = \text{constant}$. Our measurements [13] have shown that the temperatures of the maxima of ε' and ε'' , which correspond to the mechanism considered for the low-frequency relaxation, are monotonically displaced to the low-temperature region with increasing E_{\parallel} .

4. Conclusions

An analysis of the available experimental data on the influence of the bias field on the relaxation frequency of the low-frequency relaxation in $(\text{K}_{0.9}\text{Li}_{0.1})\text{TaO}_3$ crystals has been carried out. The correlation between the values of the effective field and dipole moment of the flipping polar element was determined for the first time. It is established that these polar elements are most probably pairs of the rigidly coupled dipoles (dimers) created by the off-centre Li ions. The dimer concentration and the contribution to the dielectric permittivity are estimated, and it is shown that the dimer reorientation is a catalyst for the low-frequency relaxation processes.

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