Relaxation kinetics in virtual ferroelectrics: $(K, Li)TaO_3$ crystals

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Abstract
A method for the treatment of dielectric spectra that allows calculation of electric dipole moments μ and off-centre displacements δ of Li ions in (K, Li)TaO$_3$ crystals is suggested and realized. These parameters determine characters of relaxation kinetics. The obtained estimations for μ and δ are confirmed by calculation with the Arrhenius law for the mean relaxation time and are compared with the published data.

1. Introduction

Virtual (incipient) ferroelectrics, such as KTaO$_3$ and SrTiO$_3$, are a group of ABO$_3$ perovskite crystalline materials which are promising for applications and currently being intensively studied. There are many works devoted to an analysis of phase transitions and relaxor properties which arise in the materials due to doping with small-radius impurity ions. These ions are capable of jumping between off-centre minima of a single-particle potential. In this paper we consider some results of our research on relaxation properties of the $(K_{1-x}Li_x)TaO_3$ crystals. The main attention is paid to the following problems:

(i) features of dielectric and hyper-Raman spectra which manifest themselves in relaxation processes and stem from off-centre displacements of the small-radius impurity Li ions;

(ii) an estimation of microscopic parameters of the localized ionic states, such as values of electric dipole moments and off-centre displacements of the Li ions;

(iii) kinetics of dipoles and clusters, which are induced in the (K, Li)TaO$_3$ crystals due to the off-centre arrangement of the Li ions.

A question on the potential barrier height U, the dipole moments μ and displacements δ of Li ions from the centre-symmetric positions in the (K, Li)TaO$_3$ crystals remains unsolved despite a great number of works devoted to the investigation of physical properties and phase transitions in these crystals. There are no data on direct measurements of δ and U (in view of the nearly vanishing scattering efficiency of Li for x-ray and neutron diffraction, of the necessity to use ill defined values for static ionic charges and to take into account distortions of electronic shells of the off-centre Li ions in processing NMR data etc). Therefore, only data on indirect estimations are published that are based on different theoretical models and give a large dispersion of the δ (from 0.5 to 1.6 Å [1–8]) and U values (from 170 to 2500 K

[9, 10]). The dispersion can also be connected with the presence of polarized clusters and a few relaxation and tunnelling processes with the distribution of relaxation frequencies [9, 10]. Additional difficulties stem from contradictions in experimental data and their theoretical interpretation. Apparently, it is necessary to consider first-principles calculation data as the most reliable ones (see, for example, [8]). This paper is devoted to estimation of the μ and δ values on the basis of experimental data obtained from dielectric and hyper-Raman spectra.

2. Method for treatment of dielectric spectra

As is known [2–4], a single-particle Li ion potential in the cubic paraelectric phase of the (K, Li)TaO$_3$ crystals is characterized by six off-centre minima displaced along the [100] directions. The multiminimum potential in turn causes a relaxation polarization that manifests itself in features of the dielectric and hyper-Raman spectra and can be characterized with an effective relaxation (thermal) Li polarizability $\alpha^T = \mu^2/(3k_B T)$, where k_B and T are the Boltzmann constant and absolute temperature, respectively. Let us suppose that a mean polarizability of the A cations can be written as follows:

$$\alpha_A = (1 - x)\alpha_K + x(\alpha_{Li} + \alpha^T). \tag{1}$$

The values of electronic polarizabilities for K ($\alpha_K = 1.14$ Å^3), Li ($\alpha_{Li} = 0.029$ Å^3) and O ions ($\alpha_O = 2.40$ Å^3), included in equation (1), are taken from [11].

The presence of the relaxation contribution to α_A results in a dielectric dispersion; the relaxation frequency f_r depends on the depth U of the local minima of potential energy and temperature. We treated the dielectric spectra for the (K$_{1-x}$Li$_x$)TaO$_3$ crystals with $x = 0.011$ [12], $x = 0.026$ [13] and $x = 0.050$ [14] by the use of Slater formulae [15] connecting static (ε_0, measuring at frequencies $f \ll f_r$ and incorporating a relaxation contribution) and high frequency (ε_∞, measuring at frequencies $f \gg f_r$ in the absence of the relaxation contribution) dielectric permittivities with the polarizabilities of all ionic sublattices. According to [16, 17], a deformation polarizability α_{Ta} (i.e. an electronic + ionic one) was chosen in order to reach a coincidence between the calculated and experimental values of ε_∞. The relaxation polarizability $\Delta\alpha_A = x\alpha^T$ was chosen so that the static permittivity ε_0 counted with the formulae [15] was equal to the experimental one. Simultaneously local electric fields on all ions of the crystal lattice and their ratios to the corresponding Lorentz field $E_L = (\varepsilon + 2)E/3$ were calculated (E is a macroscopic electric field strength, ε can take the values ε_∞ and ε_0). The results of our calculations are listed in table 1.

As can be seen from table 1, calculated $\mu = (0.3–0.4)$ e Å and $\delta = \mu/(se) = (0.5–0.7)$ Å (e and $s \cong 0.55$ [18] are the elementary charge and ionicity, respectively) are close to the lower boundary of the published estimations for δ (from 0.5 to 1.6 Å [1–8]). It is interesting to emphasize that the values of μ calculated by using our method for the treatment of the experimental dielectric spectra are tens times less than μ derived in [19, 20] with the Born formula for dielectric permittivity instead of the Slater one [15]. The reason for this contradiction is that the Born formula can be applied only for the crystals in which the local fields E^* on all the ions are equal to the macroscopic field E. Meanwhile, as can be seen from table 1, the local fields on different types of ions in the (K, Li)TaO$_3$ crystals strongly differ from each other. E^* on the A and O$_2$ ions are several times less than the Lorentz field E_L, while E^* on the B and O$_1$ ions are several times more than E_L. Besides, in agreement with [15], $E_A^* < 0$, i.e. $P_{Li} < 0$ and the relaxation contribution to the dielectric permittivity takes place by an indirect route as a result of interaction of the relaxation and phonon modes resulting in the increase of the local fields on the B and O$_1$ ions. The contribution of Li ion flips to the total polarization is less than 1%. Therefore the dielectric relaxation is defined by behaviour

Table 1. Experimental dielectric permittivities of the $(K_{1-x}Li_x)TaO_3$ crystals with $x = 0.011$ [12], $x = 0.026$ [13] and $x = 0.050$ [14] and calculated microscopic ionic parameters.

T (K)	ε_∞	ε_0	α^T (Å³)	μ (e Å)	δ (Å)	E_A^*/E_L	E_B^*/E_L	E_{O1}^*/E_L	E_{O2}^*/E_L
$x = 0.011$									
45	1145	4640	140.0	0.336	0.612	−0.113	4.87	3.64	0.244
						−0.171	5.07	3.77	0.204
52.5	1020	3765	148.7	0.374	0.681	−0.113	4.87	3.64	0.244
						−0.175	5.08	3.78	0.201
60	945	2495	141.8	0.391	0.711	−0.112	4.87	3.64	0.245
						−0.170	5.07	3.77	0.205
$x = 0.026$									
60	780	8230	85.7	0.304	0.553	−0.110	4.87	3.63	0.246
						−0.214	5.21	3.87	0.175
67.5	750	5650	83.6	0.318	0.579	−0.110	4.87	3.63	0.247
						−0.209	5.20	3.86	0.178
75	735	3810	83.5	0.335	0.610	−0.110	4.87	3.63	0.247
						−0.208	5.20	3.85	0.179
$x = 0.050$									
100	595	1500	42.9	0.278	0.505	−0.107	4.84	3.61	0.247
						−0.199	5.16	3.83	0.184
125	545	1040	40.1	0.300	0.546	−0.106	4.84	3.61	0.248
						−0.187	5.11	3.80	0.193
150	500	890	40.3	0.329	0.599	−0.104	4.84	3.61	0.248
						−0.186	5.11	3.80	0.194

Ratios of the effective fields E_i^* on the A, B, O$_1$ and O$_2$ ions to the Lorentz field $E_L = (\varepsilon + 2)E/3$ are calculated for ε_∞ (the first line) and for ε_0 (the second line). The ionicity $s = 0.55$ [18] is used for determination of δ.

of the total polarization but not the Li one. We think that just this circumstance stipulates a fulfillment of the Arrhenius law for the mean relaxation time τ within broad temperature and concentration ranges.

Among other effects we would like to note (i) some increase of μ and δ with increasing temperature and decreasing ion concentration and (ii) decreasing ε_∞ as compared with the static permittivity of the pure KTaO$_3$ crystals. The first effect is analogous to one observed earlier in (K, Li)Cl and (K, Li)Br crystals [21] and stems from the critical sensitivity of the off-centre displacements of small-radius impurity ions to an increase of the lattice parameter (due to weakening of short-ranged repulsive forces as contrasted to Coulomb ones). The second effect is explained by a contraction of cells, inclusive of the Li ions, that results in decreasing length of Ta–O bonding and the polarizability of the ionic displacement of the Ta ions, i.e. in a greater stiffness of a soft phonon mode.

Thus the temperature dependences of ε_0 and ε_∞ in the (K, Li)TaO$_3$ crystals are adequately described in the framework of the Slater model for all the above-considered concentrations of the Li ions.

3. Method based on using the Arrhenius law

Another approach for estimations of μ and δ proposed in [22] is based on an analytical approximation of the potential relief for the Li ions and use of parameters of the Arrhenius law for the mean relaxation time τ. The corresponding potential relief along each of the fourfold or twofold rotation axes can be well approximated by a polynomial $W = Ax^2/2 + Bx^4/4$. Then the off-centre displacement $\delta = x_0$ (x_0 is the abscissa corresponding to the potential energy

minimum), potential barrier height U and quasielastic constant k, derived from expressions for the energy W and its first and second derivatives, can be written as

$$k = -2A \qquad U = A^2/(4B) \qquad x_0^2 = -A/B = 8U/k. \qquad (2)$$

As shown in equations (2), three microscopic parameters, x_0, U and k, characterizing the single-particle potential of the off-centre Li ion can be expressed for the chosen direction through two fitting constants, A and B. This enables us to define the off-centre Li ion displacements with empirical data for U and k that are contained in the Arrhenius law for the mean relaxation time [2, 4, 23, 24]

$$\tau = \tau_0 \exp(U/(k_B T)) \qquad \tau_0^{-1} = 2f = (k/m)^{1/2}/\pi \qquad (3)$$

where f is the frequency of thermal vibrations of the Li ion (attempt frequency) at energy levels close to the local minima of the single-particle potential and m is the mass of the Li ion. For the calculation of A and B we took experimental data, $U/k_B = 1000$ K and $\tau_0 = 4.42 \times 10^{-14}$ s, from the latest work [10] on investigation of hyper-Raman spectra of the (K, Li)TaO$_3$ crystals with Li atomic concentrations between 0.008 and 0.087. These data refer to $90°$ flips of single Li dipoles becoming noncooperative at high (150–300 K) temperatures. However, in [4, 12] it is emphasized that the Arrhenius law with close U/k_B and τ_0 parameters is also applicable to a range of lower temperatures $T \geqslant (37.5–50)$ K. Using equations (2) and (3) for [110] directions we calculated $A = -29.1$ J m^{-2}, $B = 15.3 \times 10^{21}$ J m^{-4} as well as defining $k = 58.2$ J m^{-2}, and $\delta_{[110]} = 0.87$ Å. Here $\delta_{[110]}$ is a distance between the nearest local minima in the [110] direction. The corresponding Li ion displacement in the [100] direction is $\delta = x_0 = 0.61$ Å. Close results can be obtained with parameters $U/k_B = 1000$ K and $\tau_0 = (2–6) \times 10^{-14}$ s derived from dielectric [2] and NMR [4] measurements.

Equations (3) are strictly fulfilled only if the local electric field E^* on the Li ions is equal to the macroscopic field E. If all the local fields $E^* = E_L$ then τ_0 increases in proportion to the $(\varepsilon_0 + 2)/(\varepsilon_\infty + 2)$ ratio [23, 24] and becomes temperature dependent and diverged at $\varepsilon_0 \to \infty$. We consider this effect as real softening of the attempt frequency f. However an essential change of the τ_0^{-1} and f parameters can arise only if all the E^* values on all the ions of the lattice are equal to each other, that does not correspond to the real situation for perovskite-type crystals (see table 1). Moreover, there is no temperature dependence of the experimental τ_0 value derived from dielectric and hyper-Raman spectra [2, 4, 10]. Therefore we can consider our estimation $\delta \cong 0.6$ Å as a quite satisfactory one.

Our estimations of δ coincide with the corresponding values obtained in [8] and are very close to the result of [7]; however they essentially differ from $\delta = (1.26–1.35)$ Å (the polarizable point-charge model [3, 4]) and $\delta = 1.44$ Å (the shell model [6]).

4. Conclusions

Two methods are suggested and realized that enable us to determine the microscopic parameters characterizing the flips of the off-centre Li ions between the local minima of the single-particle potential in the (K, Li)TaO$_3$ crystals. It is shown that both the methods yield approximately equal estimations for the dipole moments μ and off-centre displacements $\delta = (0.5–0.7)$ Å of the Li ions and are in good agreement with the results of the recent works [7, 8]. A weak dependence of μ and δ on the temperature and concentration of the Li ions is revealed and connected with the critical sensitivity of the off-centre displacements of the impurity small-radius ions to change of the lattice parameter and thermal or concentration expansion (or contraction) of the crystal lattice.

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