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Coupling of Li⁺ relaxators to the soft mode in KTaO₃:Li

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Abstract

The complex dielectric permittivity of K_{1-x}Li_xTaO₃ (KTL) single crystals with $x = 0.006$ has been experimentally studied in detail in the temperature interval from 5 to 300 K and at frequencies from 100 Hz to 1 MHz. In agreement with previous studies, a very large effect of the Li impurities on the dielectric response, even for such a small Li concentration, is found. It consists in the appearance of a pronounced low-temperature dielectric dispersion with giant magnitude. This unusually large dielectric response cannot be caused only by the relaxation of the Li⁺-impurity off-centres themselves, because the Li concentration is too small. Also, the host lattice response itself cannot give such a large dispersion, as evidenced. We present a theoretical model, which considers the coupling of the Li⁺-related relaxators to the TO soft mode, giving a good description of the experimental data obtained.

It is known that the incipient ferroelectrics like SrTiO₃ and KTaO₃ have a very large magnitude of the dielectric permittivity at low temperatures while being in the paraelectric phase above 0 K [1]. The main feature of these crystals is the deviation of the dielectric susceptibility from the Curie–Weiss law at low T . The ferroelectric phase transition, which should appear in these crystals, from the classic point of view, is absent due to quantum vibrations of the ions.

The doping of incipient ferroelectrics with impurities can affect the dielectric permittivity behaviour strongly [2–4]. However, the dielectric response differs for different admixtures. For example, in SrTiO₃:Ca [2, 3] the dielectric permittivity increases with Ca concentration and, finally, a phase transition appears. Dielectric dispersion in SrTiO₃:Ca is practically absent. In KTL the presence of the Li impurities results in the appearance of a large relaxation polarization contribution to the dielectric permittivity, $\varepsilon'(T)$, at low T . The position of the temperature maximum in $\varepsilon'(T)$ strongly depends on the frequency of the ac external field [4]. At $x < 0.02$ and the frequency equal to 400 Hz this peak is at about 50 K. At $x > 0.02$ the increase of the Li concentration shifts the $\varepsilon'(T)$ peak position to higher temperatures [4, 5].

According to [6], the critical point, $x = 0.02$, corresponds to the case where the Li impurities coalesce each other. This coalescence leads to a very complicated picture because,

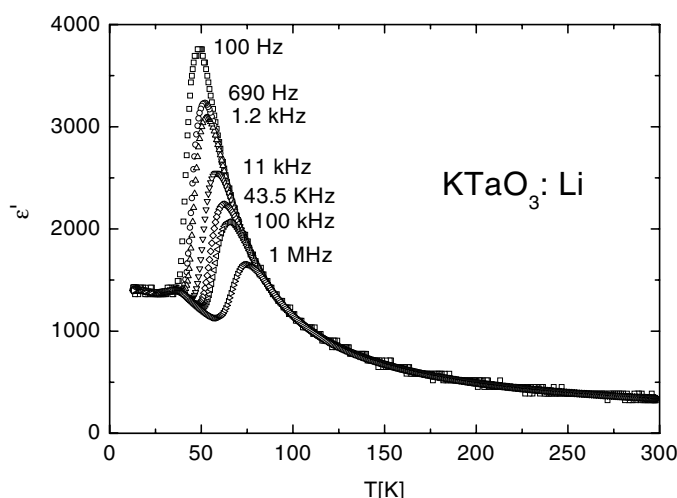


Figure 1. The dielectric permittivity ϵ' for $\text{K}_{0.994}\text{Li}_{0.006}\text{TaO}_3$ for selected frequencies, from 100 Hz to 1 MHz.

due to the random distribution of the Li ions, percolative clusters appear and finally a connected cluster arises [7]. The cluster dielectric response can be described in a similar way to the explanation of the dielectric response in relaxors [8, 9].

At the same time our knowledge about the Li^+ -centre-related dielectric contribution should be developed deeper. Here the important question is the effect of the coupling of the Li centres to the TO soft mode. This effect should be investigated in KTL compositions with Li concentrations, at least smaller than $x = 0.02$, where the TO soft mode is not completely suppressed and the mutual interaction between the Li^+ impurity centres is negligible. In the present paper we report on the results of dielectric permittivity measurements performed for $\text{K}_{0.994}\text{Li}_{0.006}\text{TaO}_3$ single crystals in the temperature interval from 10 to 300 K and at the frequencies from 100 Hz to 1 MHz. The concentration of the Li impurities in the specimens was determined by the flame emission spectroscopy method. The crystal growth technique, methods of the experimental preparation of the specimens and the dielectric-permittivity measurement set-up have been already described in [10].

Figure 1 represents the temperature behaviour of the dielectric permittivity for $\text{K}_{0.994}\text{Li}_{0.006}\text{TaO}_3$ at several selected frequencies. In the region from 47 to 80 K a pronounced dielectric relaxation peak reveals with $\epsilon'(T)$ maximum shifting to higher temperatures and decreasing in magnitude with reference ac frequency. The giant magnitude of this peak, appearing at so small an Li concentration, bears witness to the coupling of the Li-related dipoles to the soft mode.

Models which couple the relaxator mode to the soft mode were developed earlier in [11, 12] in order to describe the lattice dynamics in KDP. This coupling was employed in [5, 13] for an explanation of the ferroelectric phase transition in $\text{KTaO}_3:\text{Li}$ with $x > 0.02$. Recently this approach was used to describe experimental data on $\text{SrTiO}_3:\text{Ca}$ solid solutions [3] and the phase transition in PbTiO_3 and KNbO_3 [14]. In [15] the coupling of the modes was employed to explain a deviation from the Lyddane–Sachs–Teller relation in ferroelectrics. In [16] it was shown that the Slater model of ferroelectricity could be modified for the solid solutions by adding an averaged relaxator-type polarizability to the ordinary ionic polarizability. Here we propose an original model for treating our experimental results on the dilute $\text{KTaO}_3:\text{Li}$ system.

The main idea is to describe the dielectric response of the system as consisting of Li-related dipoles coupled to the soft mode.

The starting point of our consideration is the equation for a density matrix [11], which we employ here for the dipole-related density matrix, ρ_d ,

$$i\hbar\partial\rho_d/\partial t = [H_d\rho_d] - i\eta(\rho_d - \bar{\rho}_d)/\tau \quad (1)$$

where H_d is the dipole's Hamiltonian; $\bar{\rho}_d = \exp(-H_d/k_B T)/Sp(\exp(-H_d/k_B T))$ is the average density matrix obtained in the framework of the Boltzmann statistics; $\hbar = h/2\pi$; h and k_B are the Planck and Boltzmann constants, respectively. If one does not take into account the dipole-dipole interaction and tunnelling then the Hamiltonian for the dipoles transforms to the simplest form:

$$H_d = -2\mu E\sigma^z - \lambda P_h\sigma^z \quad (2)$$

where μ is the dipole moment of an impurity centre, E is an external field, P_h is the polarization of the host lattice, σ^z is a quasispin operator and λ is the constant coupling the dipoles to the host lattice polarization.

The substitution of (2) into (1) and performing the Fourier transformation gives:

$$-\omega\rho_d = -(2\mu E + \lambda P_h)[\sigma^z\rho_d] - i\hbar(\rho_d - \bar{\rho}_d v_d). \quad (3)$$

Here $v = 1/\tau$. For our Hamiltonian the first term vanishes. Hence

$$\rho_d = \frac{1}{1 + i\omega\tau}\bar{\rho}_d. \quad (4)$$

The polarization made by the oriented dipoles can be accounted for by the expression:

$$P_d = 2\mu n_d Sp(\sigma^z\rho_d). \quad (5)$$

where n_d is the concentration of the dipoles (this is the number of the dipoles in unit volume, $n_d = x/v_0$ with v_0 being the unit cell volume). Inserting (4) into (5) one has

$$P_d = 2\mu n_d \frac{1}{1 + i\omega\tau} Sp(\sigma^z\bar{\rho}_d). \quad (6)$$

The contribution of the dipoles to the dielectric susceptibility can be found as the derivative of this polarization with respect to E :

$$\begin{aligned} \chi_d &= \frac{1}{\varepsilon_0} \frac{dP_d}{dE} = \frac{2\mu n_d}{\varepsilon_0 k_B T} \frac{1}{1 + i\omega\tau} \left(2\mu + \lambda \frac{dP_h}{dE} \right) Sp\{(\sigma^z)^2 \bar{\rho}_d\} \\ &= \frac{2\mu n_d F(T, \omega)}{\varepsilon_0} \left(2\mu + \lambda \frac{dP_h}{dE} \right) \end{aligned} \quad (7)$$

where

$$F(T, \omega) = \frac{Sp\{(\sigma^z)^2 \bar{\rho}_d\}}{k_B T (1 + i\omega\tau)}. \quad (8)$$

Here $\tau = \tau_0 \exp(U/k_B T)$, where U is the potential barrier. The polarization of the host lattice, P_h , can be expressed through the density matrix of the ideal (defect free) crystal,

$$P_h = n_h Sp(zx\rho_h) \quad (9)$$

where z , x are the ionic charge and displacement respectively, n_h is the host-lattice ion concentration per unit volume. Here the host lattice density matrix ρ_h can be obtained from the equation for the host-lattice density matrix,

$$i\hbar\partial\rho_h/\partial t = [H_h\rho_h]. \quad (10)$$

The Hamiltonian of the host lattice is

$$H_h = H_{h0} - zEx - \lambda n_d \sigma^z P_h \quad (11)$$

where H_{h0} is the Hamiltonian in the absence of the defects and the external field E .

Substituting ρ_h into (9) by an expression deduced from equation (10) (after making the Fourier transformation and assuming that the electric field E is small) one obtains

$$P_h = (zE + \lambda z n_d \langle \sigma^z \rangle) D_h \quad (12)$$

where

$$D_h = n_h \sum x_{mn}^2 \frac{\rho_{h0}^m - \rho_{h0}^n}{\omega_{mn} - \omega}. \quad (13)$$

Here x_{mn}^2 is a matrix element of the soft mode coordinate; $\hbar\omega_{mn} = \varepsilon_m - \varepsilon_n$, ε_i is the i th eigenvalue of the Hamiltonian H_{h0} . We neglected the retardation of the soft mode but, in comparison with the retardation of the dipole relaxators, it is very small indeed.

Equation (12) makes it possible to derive a formula for the host-lattice polarization

$$\chi_h = \frac{1}{\varepsilon_0} \frac{dP_h}{dE} = \frac{z}{\varepsilon_0} \left(1 + \lambda n_d \frac{d\lambda \langle \sigma^z \rangle}{dE} \right) D_h = \frac{z}{\varepsilon_0} \left(1 + \frac{\lambda}{2\mu} \frac{dP_d}{dE} \right) D_h. \quad (14)$$

Expressing the partial susceptibilities from equations (7) and (14),

$$\begin{aligned} \chi_d &= \frac{1}{\varepsilon_0} \frac{2\mu n_d F(\lambda + 2\alpha\mu)}{\alpha - \lambda^2 n_d F} \\ \chi_h &= \frac{1}{\varepsilon_0} \frac{1 + 2\lambda\mu n_d F}{\alpha - \lambda^2 n_d F} \end{aligned} \quad (15)$$

where $\alpha = 1/zD_h$, one can find the final expression for the total dielectric susceptibility:

$$\chi = \frac{1}{\varepsilon_0} \frac{1 + 4\lambda\mu n_d F(T) + 4\mu^2 n_d \alpha(T) F(T)}{\alpha(T) - \lambda^2 n_d F(T)}. \quad (16)$$

Notice that, at $\lambda = 0$ (no coupling), this expression is reduced to a simple sum of the susceptibilities of the host lattice and dipoles: $[\varepsilon_0 \alpha(T)]^{-1} + 4\mu^2 n_d F(T)$. The only complex value in this expression is $F(T)$. This function has a Debye-type frequency dependence, $1/(1 + i\omega\tau)$, which has the obvious real, $1/(1 + \omega^2\tau^2)$, and imaginary, $-\omega\tau/(1 + \omega^2\tau^2)$, parts. The expression derived looks similar to the expressions found in [3, 14]. However, in comparison with [3] equation (16) takes into account dielectric dispersion although it does not take into account tunnelling and direct dipole–dipole interaction among the impurities. In comparison with [14] the derived expression is aimed to describe the dielectric response of solid solutions while in [14] pure crystals with mixed order–disorder and soft mode degrees of freedom were considered.

The description of the host lattice dielectric response was performed by the Barrett expression [17]

$$\alpha(T) = \frac{T_s \coth(T_s/T) - T_0}{\varepsilon_0 C} \quad (17)$$

where T_s is the saturation temperature and T_0 the classic critical temperature; C is a constant. From the experimental data it is seen that, at T below the peak position, the dielectric permittivity is considerably smaller than for pure KTaO_3 . For example, the maximal dielectric permittivity at 0 K in KTaO_3 is about 4000 whereas, in our sample of KTL under study, it is of about 1500. These data are in a good agreement with the hyper-Raman results [18] according to which the soft mode hardens due to the Li substitution. In order to take this effect into account and to subtract the host lattice contribution to the dielectric permittivity

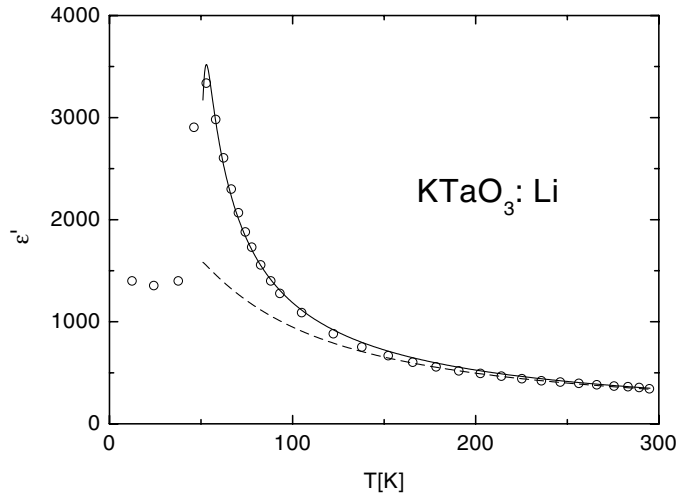


Figure 2. The fitting of the expression $\varepsilon' = 1 + \chi'$, where χ' is computed with the help of equation (16), to our experimental data (circles) taking into account the coupling of the Li relaxators to the soft mode (solid line) and without such a coupling (dashed line).

we varied the parameter T_s and found a good fit at $T_s = 48$ K and $C = 10^5$ K⁻¹. Enlarging T_s in comparison with the nominally pure KTaO₃ ($T_s = 22$ K) can have different reasons. In [18] it was shown that T_s increases with the Li content. It can be understood if one connects T_s with the soft mode frequency, ω_{c0} : $T_s = \hbar\omega_{c0}/2$ [17, 19, 20]. Indeed, due to the increase of the soft-mode frequency with the Li concentration the saturation temperature also increases. Another explanation of the increase of the saturation temperature can be related to the suppression of the dielectric susceptibility of the host lattice due to random fields produced by the dipoles.

Figure 2 shows our experimental dielectric-permittivity temperature dependence for K_{0.994}Li_{0.006}TaO₃ at $f = 400$ Hz (circles) and the respective fit of the theoretical calculation (the solid line). The impurity concentration and dipole moment were fixed at the values $n_d = 9.4 \times 10^{25}$ m⁻³ (corresponding to $x = 0.006$), $\mu = 9.6 \times 10^{-30}$ mC (corresponding to 0.6 eÅ [19]). The coupling constant was taken as $\lambda = 3.6 \times 10^{-20}$ V m² ($\lambda = \mu\gamma/3\varepsilon_0$ where $\gamma = 0.1$ [5]). A good fit was obtained for the barrier, U , being equal to about 908 K (compared with 1080 K in [21]) and $\tau_0 = 13.5 \times 10^{-14}$ s.

In order to clear up the role of the coupling constant we plotted our final expression at $\lambda = 0$ and the other parameters fixed at the same values as above (dotted line). It is seen that the vanishing of the coupling leads to a large decrease of the intensity of the relaxation peak. This implies that a reason for the existence of such a huge intensity of the relaxation peak is the coupling of the relaxators to the soft mode.

We have shown above that the model, which takes into account the coupling of the dipoles to the soft mode, is able to fit the giant magnitudes of the relaxation peak in the dielectric-permittivity experimental data. There is also another important consequence of this coupling. It can be derived from the expression (16) that the dependence of the relaxation time on temperature should deviate from the Arrhenius law and should obey the following relation:

$$\tau = \frac{e^{U/k_B T}}{2\nu} \frac{1}{1 - (1/4k_B T)(n\lambda^2/\alpha)}. \quad (18)$$

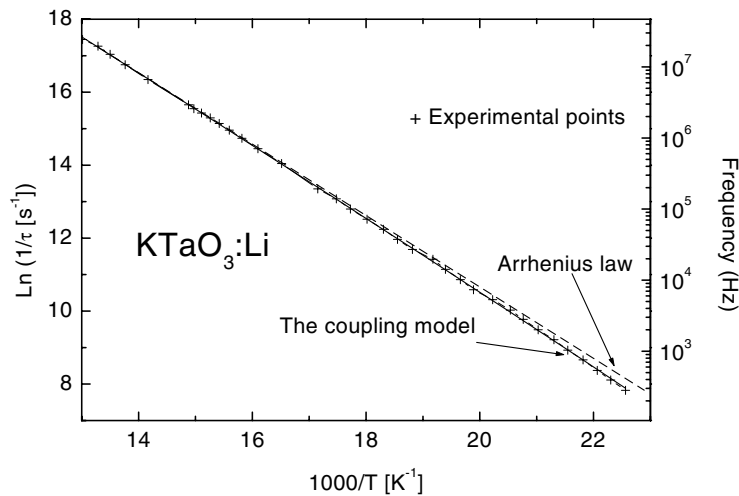


Figure 3. The comparison of the Arrhenius plot (dashed line) with the result of the model (solid line) and experiment (crosses).

Here the first factor is the conventional Arrhenius relaxation law. The temperature dependence of the second factor is critical. As a result, the relaxation time diverges when the denominator in (18) vanishes. By using (17) expression (18) takes the form

$$\frac{1}{\tau} = \frac{e^{-U/k_B T}}{\tau_0} \left[1 - \frac{A^2}{T(T_s \coth(T_s/T) - T_0)} \right] \quad (19)$$

where $A^2 = n_d \lambda^2 C \epsilon_0 / 4k_B$. We plotted the experimental points for the relaxation time in KTL with $x = 0.006$ versus inverse temperature (figure 3). For the fit we have used the same values of the parameters as above and obtained good agreement between the experiment and theory. It is seen that the deviation from the Arrhenius law (dashed line) becomes larger when upon lowering the temperature one is coming closer to the temperature of the relaxation peak position. From this point of view it would be better to call this peak a cooperative one than a relaxation peak. The agreement between theory and experiment makes clear how important coupling of the dipoles to the soft mode is in dilute KTL.

Finally we suggest that the giant dielectric polarization response in dilute KTL is caused by the strong interaction between the relaxators and soft mode. We have shown that by taking such a coupling into account the experimental data can be described quantitatively in a straightforward way.

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