Comment on "Dielectric behavior of paraelectric KTaO$_3$, CaTiO$_3$, and (Ln$_{1/2}$Na$_{1/2}$)TiO$_3$ under a dc electric field"

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Chen Ang, Bhalla and Cross [Phys. Rev. B 64, 184104 (2001)] have studied the low-frequency (20 Hz – 100 kHz) dielectric dispersion of the KTaO$_3$ crystal under a dc electric field. Performing fits of the electric field dependence they came to conclusion that an appreciable contribution to the dielectric permittivity originates from polar clusters. In this Comment we show that the dielectric permittivity at low frequencies (100 Hz – 1 MHz) equals to that in the THz region, close below the polar phonon response. This excludes the possibility of any appreciable dielectric dispersion due to polar clusters. In addition, we demonstrate that correct treatment using Landau-Ginzburg-Devonshire theory allows to fit the electric field dependence of the dielectric constant without assuming any polarization mechanism besides the polar phonon modes.

In the following we will show that our recent FIR and LF dielectric measurements of KTO exclude the possibility of any appreciable contribution to the LF permittivity besides the contribution of the soft phonon mode. Moreover we will demonstrate that a correct treatment using the Landau-Ginzburg-Devonshire thermodynamic theory allows to describe the field dependence of the dielectric constant in KTO without using additional Langevin-type terms.

Our measurements have been performed on nominally pure KTO single crystals. The samples were prepared in the form of thin <001>-oriented plane-parallel plates with dimensions of 7 x 7 x 0.2 mm$^3$. LF dielectric measurements were carried out using a HP 4192A Impedance analyzer in the frequency range 100 Hz – 1 MHz with gold electrodes deposited on the main surfaces of the sample. The FIR reflectivity was measured with Bruker IFS 113v Fourier Transform spectrometer in the range 30 – 650 cm$^{-1}$. The complex dielectric function in the frequency range 5 – 30 cm$^{-1}$ was obtained by means of time-domain THz transmission spectroscopy on a 65 µm thick plane-parallel sample. The frequencies of the three polar phonon modes and their contribution to the dielectric function were obtained from the fit to the FIR reflectivity using the factorized form of the model dielectric function combined with the directly measured values of the THz complex permittivity. The temperature dependence of the soft-mode frequency was found to be in perfect agreement with the hyper-Raman data.

In Fig. 1 the measured permittivity at 43.5 kHz is compared with the low-frequency limit of our fitted FIR dielectric function. The permittivity data from Ref. 6 are also added for comparison. One can observe good agree-
derivative dc bias field, one has to use Eq. 3 to calculate the permittivity of vacuum. To calculate the permittivity within the damped harmonic oscillator model, Fleury and Worlock [3,4] use two independent parameters \( \xi \) and \( \lambda \). Let us expand the crystal free energy per unit volume in a power series of lattice polarization:

\[
G = G_0 + \frac{1}{2} \chi(T)(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4} \xi(P_x^4 + P_y^4 + P_z^4) + \frac{1}{2} \xi'(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) + \frac{1}{6} \zeta(P_x^6 + P_y^6 + P_z^6) + \text{other sixth–order terms} + \ldots \tag{2}
\]

In our case polarization has only one component directed along the z-axis \( P_z = P_y = 0 \). Thus we can obtain relation between the electric field and polarization:

\[
E_z = (\partial G/\partial P_z)_T = \chi(T)P_z + \xi P_z^3 + \zeta P_z^5 + \ldots \tag{3}
\]

which is a special case of the general relation for arbitrary polarization in Ref. 10. Then one can derive the expression for the inverse susceptibility:

\[
\left( \frac{1}{\varepsilon_0(\varepsilon(T, E) - 1)} \right)_z = \partial E_z/\partial P_z = \chi(T) + 3\xi P_z^2 + 5\zeta P_z^4 + \ldots \tag{4}
\]

Here \( \chi(T) = 1/\varepsilon_0[\varepsilon(T, 0) - 1] \) is the inverse susceptibility in the zero bias field and \( \varepsilon_0 = 8.85 \cdot 10^{-12} \text{ F/m} \) is the permittivity of vacuum. To calculate the permittivity under dc bias field, one has to use Eq. 5 to calculate the polarization and then insert it into Eq. 3. The calculations should be performed numerically because Eq. 3 is a nonlinear polynomial equation of the 5-th order. Therefore the analytical expression given in Ref. 6 cannot be valid for highly anharmonic crystals and can be applied only in the weak field approximation. This approximation apparently holds in the case of CTO and LNTO because of their weak nonlinearity for bias fields \( E < 60 \text{ kV/cm} \). However, in the case of KTO the lattice anharmonicity is essential. The fit using Eq. 3 and 4 of KTO permittivity under the dc electric field at 14 K taken from Ref. 6 (the first run of measurements) is shown in Fig. 2. The fit uses two independent parameters \( \xi = 10^{10} \) and \( \zeta = 10^{11} \) in SI units and the value \( \epsilon(14 \text{ K}, 0) = 2821 \) taken from Ref. 6. The fitted nonlinear coefficients are in reasonable agreement with the previously published data (see Ref. 10 and references therein). Fig. 2 demonstrates that the expansion up to the 6-th order in Eq. 2 is sufficient to ensure a good agreement between the theory and experiment.

The critical limit for the weak field approximation can be found from the condition that 4-th and 6-th order terms in Eq. 2 are small compared to the quadratic term:

\[
\xi P_z^2 + \zeta P_z^4 = \lambda \chi, \tag{5}
\]

where \( \lambda \ll 1 \) is a dimensionless constant. For the typical values of nonlinear coefficients \( \xi \) and \( \zeta \) we can neglect the 4-th order term in Eq. 5 and using Eq. 3 we obtain

\[
E_{cr} = \chi \sqrt{\frac{\lambda \chi}{\xi}}. \tag{6}
\]

Using our fit parameters for KTO and \( \lambda = 0.1 \) we calculate \( E_{cr} \approx 1.3 \text{ kV/cm} \). One can see that this value is much smaller than the highest dc electric field in Ref. 6 (60 kV/cm).

It is believed that polar nano-clusters are induced by unavoidable dipolar impurities in nominally pure KTO.
The presence of such clusters appears in the LF dielectric spectra of KTO as a universal low-temperature dielectric dispersion with thermally activated behavior. Below 30 K this dielectric dispersion shifts below the frequency range of conventional LF dielectric spectroscopy. Dielectric spectroscopy can only establish that the contribution to permittivity of polar clusters is very small comparing to the phonon contribution above 30 K and cannot be observed in LF dielectric spectra below 30 K. On the other hand, the polar clusters can be detected by light scattering as it has been done in Raman and hyper-Raman scattering experiments. These experiments, however, bring no information about the dynamics of the clusters because their relaxation is quasi-static comparing to the frequencies resolved in the light scattering experiments. The local lattice symmetry breaking due to the polar clusters relaxes the selection rules and induces activation of new lines. These changes are in agreement with existence of the polar clusters and do not contradict with our dielectric spectroscopy results.

Taking into account all the mentioned arguments, we can conclude that the estimated size of polar clusters found in Ref. 6 does not have any reliable physical background and its possible correspondence with the Raman results is accidental.

Analysis of the field dependence of permittivity using equation similar to Eq. 1 was previously applied also to Sr$_{1-x}$Ca$_x$TiO$_3$ system where, due to the Ca-doping, appreciable dielectric dispersion indeed exists. However, the applied electric fields were much smaller ($E < 1$ kV/cm) than those in Ref. 6. Estimation of the critical electric field from Eq. 6 gives for STO $E_{cr} \sim 0.2$ kV/cm (nonlinear parameters are taken form Ref. 10). Thus even 1 kV/cm field can introduce some error if one uses Eq. 1. In our opinion, the correct thermodynamic approach described here is always preferable for the analysis of nonlinear behavior under strong electric fields.

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