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Low-frequency dispersion of the dielectric permittivity in a triglycine sulfate crystal subjected to nonequilibrium conditions

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It was shown that if a short-circuited single-domain triglycine sulfate (TGS) crystal is subjected during a certain time to a steady-state temperature gradient, then it is nonuniformly polarized. The origin of this polarization is a nonuniform electric field which in turn derives from the nonuniform temperature gradient. These conclusions were derived from temperature measurements of the dielectric permittivity of TGS crystal. The exhibited low-frequency (within kHz range) dispersion of the dielectric permittivity can be explained by the relaxation of the bidomain wall inside the crystal.

Usually the measurements of the dielectric properties of ferroelectric crystals are performed under well-defined thermodynamic equilibrium conditions, i.e., without any fluxes like heat flow and so on. Strukov *et al.*,[1] inspired by Marvan's theoretical paper,[2] experimentally studied the changes of the basic macroscopic properties of a ferroelectric crystal during the change of thermodynamic conditions from thermodynamic equilibrium to nonequilibrium, i.e., when a temperature gradient was applied. The author gave a simple phenomenological description of some properties of ferroelectrics subjected to a steady-state temperature gradient during suitable measurements.[3] As it was shown, the obtained model confirmed the experimental data.

In this paper we investigate the dielectric properties of ferroelectrics subjected to the nonequilibrium conditions, i.e., when a temperature gradient was applied to the sample during some time before appropriate measurements. It was shown that the temperature gradient imposed to the crystal modifies the phase transformation. It was assumed that the origin of these changes is the thermally generated electric field (TGEF) coming from the temperature gradient according to the following scheme: It is well known that inhomogeneous heating of ferroelectrics is always associated with a bound charge[4]

$$\rho = -\mathrm{div}\mathbf{P}(T) = \boldsymbol{\lambda}\cdot\mathrm{grad}(T) , \tag{1}$$

where $\boldsymbol{\lambda}$ is the pyroelectric coefficient. According to Poisson's equation a bound charge ρ generates inside the sample an inhomogeneous distribution of electric potential

$$\Delta\Phi = -\frac{\rho}{\epsilon_0\epsilon}, \quad \Delta\Phi = \frac{1}{\epsilon_0\epsilon}\boldsymbol{\lambda}\cdot\mathrm{grad}T , \tag{2}$$

where ϵ and ϵ_0 are the dielectric permitivity of the crystal and of the vacuum, respectively. Then of course the suitable electric field can be written as

$$E = -\mathrm{grad}\Phi , \tag{3}$$

and called the thermally generated electric field. Hadni[5,6] first pointed out the importance of this field and used it to explain the microdomain switching in triglycine sulfate (TGS) crystals illuminated by a strong focused laser beam (see Refs. 3 and 4). The solution of Eq. (2) is particularly simple in the case of a short-circuited single-domain ferroelectric crystal plate, in which the upper surface is uniformly heated under static conditions, and the lower one is kept at constant temperature. Then inside the crystal arises a constant (position-independent) static temperature gradient. The suitable one-dimensional (1D) Poisson equation should be written as

$$\frac{d^2\Phi}{dy^2} = \frac{1}{\epsilon_0\epsilon}\lambda\,\mathrm{grad}T \tag{4}$$

and solved for the following boundary conditions corresponding to a short-circuited sample:

$$\Phi(y=0)=0 ,$$

$$\Phi(y=d)=0 ,$$

where y denotes the direction of the spontaneous polarization P_s, and d is the thickness of the sample. Then the solution of (4) can be found

$$\Phi(y) = \frac{\lambda}{2\epsilon_0\epsilon}\mathrm{grad}(T)(y^2 - yd) , \tag{5}$$

and next according to Eq. (3), the thermally generated electric field is

$$E(y) = \frac{\lambda}{2\epsilon_0\epsilon}(d-2y)\mathrm{grad}(T) . \tag{6}$$

We can see that a uniform temperature gradient causes an inhomogeneous electric potential $\Phi(y)$ and electric field distribution $E(y)$ in the crystal. Figure 1 schematically shows the calculated electric potential (5) and TGEF (6) for $\lambda < 0$ and $P_s > 0$. This electric field is polarizing in the upper part of the crystal, while in the lower part it is depolarizing with respect to the spontaneous polarization P_s. As it follows from the calculations, the local strength of this field can reach a value of the order

MV m^{-1} depending on the magnitude of the temperature gradient. If a sample is subjected to this field during a certain time, then we can expect significant changes in its domain structure. It is probable that in the part of the sample where the TGEF is depolarizing, the switching of the spontaneous polarization occurs. Thus, we can expect a reciprocal domain configuration of the "head to head" type which is proper for semiconducting ferroelectrics in their equilibrium state. It was assumed that such a domain structure should give a contribution to the dielectric response. In order to check the assumption, the following experiment was conducted: A single-domain TGS crystal plate of thickness $d=2$ mm cut perpendicularly to the polar axis was electroded using silver paste and colloidal graphite. The electrically short-circuited sample was mounted on a massive heat sink kept at constant temperature (room temperature) while the end was heated using a 20-mW ir-diode-laser beam giving a temperature difference about 0.3 °C between the upper and lower surfaces of the crystal. After a lapse of some hours the heating of the crystal was switched off, and next the sample was connected to a full computerized HP-Capacitance Bridge measuring the dielectric permittivity versus the temperature at three frequencies 10, 20, and 40 kHz simultaneously.

Figure 2 shows the results of this experiment. From Fig. 1 it can be seen that the dielectric response of the crystal is strongly influenced by its history, i.e., the crystal "remembers" that is was subjected to a temperature gradient. Curve 1, $\omega=10$ kHz, in Fig. 1 giving a temperature dependence of the dielectric permittivity for $\omega=10$ kHz is smeared in comparison to the corresponding curve obtained for a virginal sample which was not subjected to a temperature gradient. This curve 1 very closely resembled the changes in the static permittivity of a ferroelectric crystal measured in a weak alternating field in the presence of an external electric dc bias field. Further, it can be easily noted that the dielectric permitivity exhibits dispersion, i.e., the shape of the suitable curves depend on frequency of the measuring field. So for $\omega=20$ kHz (see curve 2), we can observe at the transition point a minimum instead of a maximum, which becomes deeper for $\omega=40$ kHz (see curve 3). In many ways this situation resembles the well-known critical slowing down observed in order-disorder-type ferroelectrics at very high frequencies. In the case of TGS crystals the suitable data were reported by Luther and Müser (see Ref. 7). It is well known that the response of a ferroelectric to an applied electric field exhibits a time lag which causes the dielectric dispersion in a certain frequency region. This dispersion can be described by the following Debye-type expression:[8]

$$\epsilon(\omega)-\epsilon_\infty=\frac{\epsilon_0-\epsilon_\infty}{1+(\omega\tau)^2} . \tag{7}$$

Here ω is the angular frequency of the applied ac electric field, ϵ_0 and ϵ_∞ are the dielectric permittivity at $\omega=0$ and $\omega=\infty$, and τ is the relaxation time.

One can see that at the transition point T_c, where the relaxation time tends to infinity, the dielectric permitivity should take a minimum, whereas at $T_1<T_c$ and $T_2>T_c$ it should have a maximal value for which the condition $\omega\tau=1$ is fulfilled. Moreover, the distance between these maxima depends on the measuring frequency. So we can see that the existence of a minimum in the temperature dependence of the dielectric permitivity means that the polarization cannot follow the applied measuring field of any frequency, except the zero one. As it seems, the experimental results given in Fig. 2 can be described by this model. However, the problem is that the dispersion takes place for very low frequencies within the kHz range

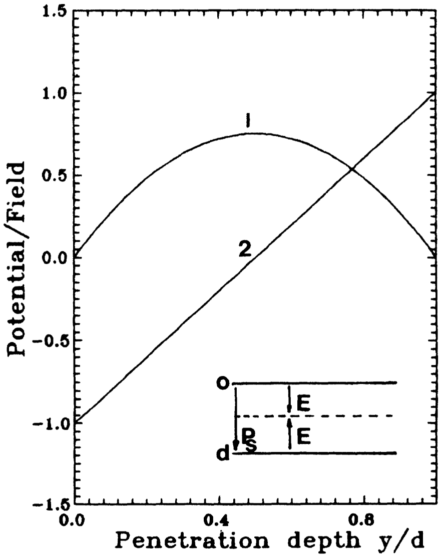

FIG. 1. The distribution of the electric potential, curve 1, and electric field, curve 2, in the crystal for $\lambda<0$ and $P_s>0$.

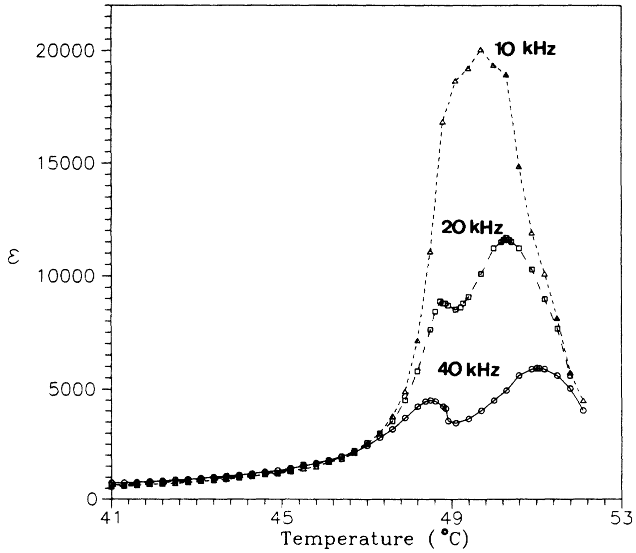

FIG. 2. The dielectric permittivity of the TGS crystal vs temperature.

which is opposite to results reported in Refs. 7 and 8. Such low-frequency dispersion of the dielectric permittivity can be explained rather by the relaxation of the domain wall inside the crystal. The reason for it could be as follows. Since the single-domain crystal was subjected during a certain time to the TGEF given by Eq. (6), one can assume that it was nonuniformly polarized in the following manner: the upper part of it was polarized with a nonuniform electric field parallel to the direction to the spontaneous P_s, whereas the lower one was depolarized. Thus, it is possible that the resulting domain structure of the crystal is similar to the one shown in Fig. 1, i.e., a reciprocal domain structure of "head to head" type. Such a domain wall needs an enormous electrical free charge generating a suitable electric field inside the crystal; therefore, it can be observed only in semiconducting ferroelectrics. However, in our case a similar electric field was created by a temperature gradient. Since this field is nonuniform, one can expect that the crystal will be polarized nonuniformly, too. It is well known that the energy of a polarizable particle with permanent and induced dipole moments in a nonuniform electric field can be written as[9]

$$W(y)=-\mathbf{p}\cdot\mathbf{E}(y)-\tfrac{1}{2}\mathbf{E}(y)\cdot\overleftrightarrow{\alpha}\mathbf{E}(y)\ . \tag{8}$$

This shows that the energy of the particle is a function of the position in the crystal. Thus, the force in the y direction, exerted by the electric field E_y (in our case the thermally generated electric field) on a particle with a permanent dipole moment p and the scalar polarizability α, is obtained by taking the derivative of Eq. (8)

$$\mathbf{F}(y)=p\frac{\partial\mathbf{E}}{\partial y}+\tfrac{1}{2}\alpha\frac{\partial^2\mathbf{E}}{\partial y}\ . \tag{9}$$

We can see from (9) that the translational force is proportional to the gradient of the electric field $E(y)$ and will be equal to zero in an uniform field. Putting expression (6) into (9) we obtain

$$F(y)=p\ \mathrm{grad}(T)\frac{\lambda}{\epsilon_0\epsilon}-\tfrac{1}{2}\alpha\frac{\lambda^2}{\epsilon_0^2\epsilon^2}(d-2y)\mathrm{grad}T\ . \tag{10}$$

This describes the nonuniform deformation forces in the crystal when the temperature gradient is applied. The first term is the force which acts on the permanent electric dipoles, whereas the second one is the force acting on the induced dipole moments. It is clear that the force given by (10) describes the nonuniform electrostriction caused by attraction among the in line permanent dipoles and the dipoles induced by field (6). In the absence of the temperature gradient, the above forces vanish. As it seems, just this interaction assures the above postulated bidomain state in the TGS crystal.

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