Selective heating of the ferroelectric film soft mode phonons

A.V. Prudan
Electrotechnical University, Prof. Popov str. 5, 197376, St. Petersburg, Russia

A.V. Mezenov
Electrotechnical University, Prof. Popov str. 5, 197376, St. Petersburg, Russia

S.A. Ktitorov
A.F. Ioffe Physicotechnical Institute, Polytechnicheskaja str. 26, 194021 St. Petersburg, Russia; Electrotechnical University, Prof. Popov str. 5, 197376, St. Petersburg, Russia

Results of the experimental study of the electromagnetic pumping of frequency 0.3 THz upon the soft mode phonons in the (Ba, Sr)TiO$_3$ film are presented. Some features of the phonon state are revealed using the capacitor thermometer and the thermocouple. The soft mode phonon overheating estimated comparing changes of the planar capacitor capacitance was observed to be quite significant.

I. INTRODUCTION

The dielectric susceptibility $\epsilon$ of a ferroelectric is determined by the phonon spectrum of the crystal and by the phonon state distribution functions (outside the harmonic approximation) [1]. This leads to a temperature dependence of $\epsilon$ in the equilibrium case. However, there exists in principle a possibility to create an nonequilibrium phonon distribution that can allow us to control the crystal properties with small delay and applying rather weak controlling fields. In particular, a nonequilibrium state can be created with the high-frequency electromagnetic radiation, which interacts selectively with the soft mode phonons. As a precedent we can refer to the discussion of possible stimulation of the superconductor transition by the electromagnetic radiation [2].

A study of the perovskite ferroelectrics with the IR and Raman spectroscopy methods gives information on the frequency and attenuation of the soft mode and reveals dependence of these parameters on the structure defects and the chemical content fluctuations [3], [4], [5], [7]. Characteristic frequency of the dielectric susceptibility (and, therefore, of the soft mode) in the SrTiO$_3$ films measured at the room temperature lies within the range of (0.4 ÷ 0.7) THz). The dispersion frequencies observed in the Ba$_x$Sr$_{1-x}$TiO$_3$ solid solution films lie in the same range [6]. The relaxation time $\tau$ and the inverse soft mode frequency $\omega_0^{-1}$ for the oxygen-octahedral ferroelectrics measured by the IR spectroscopy method are of the same order: $\omega_0 \tau \sim 1$. This product is small ($\omega_0 \tau < 1$) near the phase transition point: overdamped mode. As the temperature shifts away from this point, the inequality reverses its sign that indicates a transition of the soft mode into the underdamped state. Notice that films have a wider temperature range, where the soft mode is overdamped in comparison with monocrystals [7]. Theory predicts [1] that at approaching the phase transition point in monocrystals $\omega_0^2$ tends to zero as $(T - T_c)$, while $\tau(T) \sim \frac{aT}{\hbar \omega_0} + b \left(\frac{T}{\hbar \omega_0}\right)^2$. Here $a$ and $b$ are parameters of the material [1].

Results of the study of the soft mode phonons in the ferroelectric thin film by the electromagnetic pumping of the one-millimeter band are presented in this paper.

Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ solid solution film was deposited on the dielectric substrate. Within the framework of the harmonic approximation an ideal interface between the film and the substrate is practically transparent for the acoustic phonons (neglecting rather weak reflection due to the sound velocities mismatch) and ideally reflecting for the soft mode phonons. Taking into account the anharmonicity and violation of the quasimomentum conservation law in the vicinity of the interface leads to conclusion that the energy exchange between the phonon subsystems is anomalously intensive in this domain. The substrate plays a role of the thermostat due to good thermal contact with the environment. The thermal capacity of the thermostat $C$ essentially exceeds one of soft mode phonon subsystem $C_s$. Smallness of $C_s$ in comparison with $C$ provides a necessary condition for overheating of the soft mode subsystem by the pumping field, while other oscillatory modes remain practically unperturbed. Preliminary analysis shows that a condition of the soft mode overheating reads:

$$\frac{C_f}{C_s} \cdot \frac{\tau_s}{\tau_f} > 1,$$

where $C_s$ and $C_f$ are respectively the critical softmode and noncritical subsystem thermal capacities; $\tau_s$ and $\tau_f$ are respectively the characteristic times for energy exchange between the modes and the film and the substrate. The
integral parameters $C_f$ and can be measured and calculated with good accuracy. Two other values $C_s$ and $\tau_s$ are very difficult to determine. The uncertainty stems mainly from unknown phonon-phonon and phonon-impurity interaction constants. Comprehensive study of microscopic interaction mechanisms is necessary.

II. EXPERIMENT

A schematic drawing of the experimental setup is depicted in fig. 1.

It includes the planar capacitor based on the Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ solid solution film 12 $\mu$m in thickness deposited on the MgO single crystal substrate 1.5 $\times$ 1.0 $\times$ 0.5 mm in size. Two electrodes are separated by the narrow gap of 15 $\mu$m. A miniature chromel-copel thermocouple having one of the junctions in good thermal contact with the capacitor electrode, was used for measuring the multilayered structure temperature. The temperature of the soft mode subsystem was monitored measuring the capacity and using the known capacity dependence on the totally equilibrium temperature.

Experimental data on the temperature dependence of the inverse capacity of the samples under the study can be approximated with a good accuracy by the linear function $C^{-1} \propto (T - T_C)$ in the temperature range 270 $\div$ 340 K with $T_C = 210K$. Measurements carried out with a use of the RLC-meter E7-12 provided better than 8% (for $\Delta T > 2K$) precision of measurements of the temperature increase induced by the pumping of the critical phonon subsystem. The source of the electromagnetic radiation created the energy flux in the direction from the substrate external surface to the ferroelectric film (fig. 1). The MgO slab of the volume 1.5 $\times$ 1.0 $\times$ 0.5 mm$^3$ had a rich spectrum of resonance frequencies for the electromagnetic field of the millimeter band. Results of measurement of frequency dependence of the transmittance coefficient $K$ (fig. 2 a) and the pumping induced overheating $\Delta T$ in the cases of the MgO slab with and without the ferroelectric film are presented in fig. 2.

Measurements of the equilibrium temperature increase were carried with a use of the thermocouple at the condition of a weak thermal contact of the sample with the thermostat. Notice that the frequency dependence $\Delta T(\omega)$ characterizes a spectral behaviour of the integral absorption coefficient of the whole object under the study.

Comparison of the data presented in fig. 2 b shows that (i) presence of the ferroelectric film leads to an essential increase of the system absorptivity; (ii) the overheating $\Delta T(\omega)$ (see fig. 2 b) and, therefore, the ferroelectric film absorption coefficient depend on the pumping radiation frequency. The measured frequency dependence of the overheating $\Delta T(\omega)$ (fig. 2 b) characterizes an integral effect of the frequency-dependent absorption of the pumping energy by the soft mode at the condition of the system low Q-factor resonance. Electromagnetic pumping with the intensity about 6 mW/mm$^2$ induces a decrease of the system capacity. The capacity change magnitude depends on the pumping frequency and has a maximum, where more, than 20% decrease of the capacity occurs. Notice that the completely equilibrium overheating of the capacitor could induce only 10% decrease of the capacitance. Making the consequent analysis easier, we presented in fig. 3 the experimental data as an increase of the structure temperature measured simultaneously with the thermocouple $\Delta T$ and the capacitor thermometer $\Delta T_s$.

Both of the thermometers detected a nonmonotone pumping frequency dependence of the temperature and demonstrated an essential difference of their data: $\Delta T_s > \Delta T$. Maximum temperature difference reached 10 degrees. Such significant temperature difference cannot be traced back to the temperature difference between the thin film absorbing the pumping energy and the substrate. Numerical consideration of the locally equilibrium temperature in such a structure predicts significantly lower temperature difference between the film and the substrate.

III. DISCUSSION

This contradiction can be resolved assuming that the pumping induces an increase of the soft mode phonon occupation numbers exceeding the equilibrium values. These occupation numbers can be expressed in terms of the soft mode partial temperature $T$. As it follows from eq. (1), overheating of the softmode in the ferroelectric is possible if $C_s/C_f < \tau_s/\tau_f$. This inequality must be made stronger taking into account magnitudes of the pumping power and the temperature changes. We believe that the heat capacitance of the soft mode subsystem can be anomalously small
in comparison with one for the entire system. The relative number of the excited oscillator states near the soft mode band bottom reads

$$\frac{\delta N}{N} = \left(\frac{\omega_m - \omega_0}{\omega_0}\right)^{3/2} \left(\frac{\omega_0}{\omega_l}\right)^3,$$

where $\omega_m$ is the pumping frequency; $\omega_0$ is the soft mode band lower frequency at the fixed macroscopic state; $\omega_l$ is longitudinal phonon frequency (Debye frequency).

It was assumed that the leading contribution to this temperature dependence came from the soft mode phonon distribution and, therefore, the capacity dependence on the soft mode partial temperature in the case of the partial equilibrium was qualitative similar. Generation of the excess nonequilibrium soft mode phonons leads to a shift of the soft mode eigenfrequencies $\omega_t(k)$ in the vicinity of the spectrum bottom and, therefore, to a change of the dielectric susceptibility:

$$\epsilon^{-1}(k = 0, \omega = 0) \sim \omega_t^2(0) + \delta \omega_t^2(0).$$

A deviation of the squared frequency $\delta \omega_t^2(0)$ can be estimated using the self-consistent field approximation:

$$\delta \omega_t^2(q) = \sum_{j,k} V_{ijk} \frac{\delta n_{jk}}{\omega_j(k)},$$

where $\delta n_{jk}$ is the excess population number of the nonequilibrium phonons of the spectrum branch $j$ and the wave vector $k$, $V_{ijk}$ is the quartic anharmonic interaction constant. The pumping electromagnetic field and the anharmonic phonon-phonon interaction establish nonequilibrium state of the critical phonon subsystem belonging to a rather narrow spectral domain near the dispersion curve $\omega(q)$ bottom $q = 0$. At high temperatures $\hbar \omega(0) \lesssim k_B T$ the nonequilibrium component $\delta n_t$ of the phonon distribution function can be written in the form

$$\delta n_q = \begin{cases} \frac{k_B (T - T_0)}{\hbar \omega(q)}, & \text{if } \omega(q) < \omega_m \\ 0, & \text{if } \omega(q) > \omega_m \end{cases}$$

where $T$ is the partial temperature of the nonequilibrium phonon subsystem; $T_0$ is the temperature of thermostat formed by noncritical phonons; $\hbar \omega_m$ is the cut-off energy separating the excited subsystem. If the pumping frequency $\omega$ exceeds the soft mode lower frequency $\omega_l(0)$, then nonequilibrium phonons are located mainly between these frequencies. The expression (1) shows that the temperature like parameter $T$ can be used as a measure of deviation of the soft mode phonon subsystem from the equilibrium state. However, the parameter $T$ cannot be understood too literally as a temperature: it is rather a parameter characterizing the excess population of the excited phonon states. Firstly, the local equilibrium conditions, necessary for the quasihydrodynamical approximation to be valid, are not satisfied; secondly, the tail of the distribution is not determined by the parameter $T$. The overheating $T - T_0$ is proportional to a difference of the susceptibilities $T - T_0 \propto \epsilon^{-1} - \epsilon_0^{-1}$, which can be easily measured. The partial temperature can be determined from the energy balance equation

$$P = C_s \frac{T - T_0}{\tau_e},$$

where $\tau_e$ is the characteristic time of the energy exchange between the hot phonons and the thermostat; $C_s$ is the partial thermal capacity of the excited subsystem. The energy balance equation (5) has significantly wider domain of applicability, than the quasi-hydrodynamic approximation equations including the energy transport equations.

### IV. CONCLUSION

In conclusion, the effect of the electromagnetic pumping on the low-frequency dielectric susceptibility of the thin ferroelectric film is experimentally observed. A theoretical description of this phenomenon in terms of the soft mode phonon overheating has been presented.

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FIG. 1: Experimental setup for the selective overheating of the soft mode. 1 – ferroelectric film; 2 – dielectric substrate; 3 – electrodes of the planar capacitor; 4 – thermocouple; k – wave vector of the electromagnetic pumping
FIG. 2: Dependence of the transmission coefficient $K(f)$ and the system temperature without (1) and with the ferroelectric film (2) on the pumping radiation frequency. MgO substrate (1.5x1.0x0.5) mm$^3$; ferroelectric Ba0.4, Sr0.6)TiO3; environment temperature $T = 293$ K.
FIG. 3: The capacitor temperature change due to the electromagnetic pumping as a function of the frequency. (1): capacitor thermometer data; (2): thermocouple thermometer data.
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