06

Flexodielectric Effect in $SrTiO_3$ Single Crystals

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The dielectric response to non-uniform spherical bending deformation in thin strontium titanate single-crystal plates was studied to identify the non-linearity of flexoelectric electromechanical interaction. The direct influence of non-uniform deformation on the value of dielectric susceptibility was shown.

Keywords: Dielectrics, Flexoelectric effect, Ferroelectrics, Strontium Titanate.

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1. Introduction

Flexoelectric effect is of great interest as an electromechanical phenomenon that is most strongly pronounced in dielectric and semiconductor crystals and films of micro- and nanoscopic scales. Prospects of practical utilization effect in such fields as integral electronics, microelectromechanical systems (MEMS) and straintronics [1–3] motivate theoretical and experimental studies. Phenomenological description of flexoelectricity on the basis of thermodynamic Landau theory is published in [1], where an equation of thermodynamic potential density is provided to establish the relation between the dielectric polarization P, electric field E, mechanical stress σ and their gradients:

$$\Phi = \frac{\chi_{ij}^{-1}}{2} P_i P_j + \frac{c_{ijkl}}{2} u_{ij} u_{kl} + \frac{g_{ijkl}}{2} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l} - \frac{f_{ijkl}}{2} \left(P_k \frac{\partial u_j}{\partial x_l} - u_{ij} \frac{\partial P_k}{\partial x_l} \right) - P_i E_i - u_{ij} \sigma_{ij}, \quad (1)$$

Here, χ is the dielectric susceptibility, c_{ijkl} is the elasticity tensor, coefficients g_{ijkl} and f_{ijkl} of terms containing the gradients bear the names of flexoelectric interaction tensors. One of the electromechanical equations derived from equation (1) describes the direct flexoelectric effect, from which it follows that a strain gradient, through the flexoelectric coupling, has the same effect as an electric field that polarizes the dielectric [1]:

$$\chi_{ij}^{-1} P_j = E_i + f_{klij} \frac{\partial u_{kl}}{\partial x_j}. \quad (2)$$

Flexoelectric properties of crystals are characterized more often using flexoelectric coefficients, connection of which with the flexoelectric interaction tensors is defined by the following equation [1]:

$$\mu_{klij} = \chi_{is} f_{klsj}. \quad (3)$$

In equation (3), direct dependence of μ on χ means that the flexoelectric response is most strongly pronounced in materials with high dielectric susceptibilities, for example, in ferroelectric materials [1]. However, it is well known that dielectric response becomes nonlinear to an electric field and other impacts, in particular, in the vicinity of phase transitions [4]. This implies that higher-order contributions of P, strain u and of their derivatives with respect to coordinates are included in the thermodynamic potential density equation (1). Such approach might be illustrated by description of a flexocaloric effect in $BaTiO_3$ and $SrTiO_3$ crystals [5] where the thermodynamic potential (1) also includes terms with an order parameter up to a term to the sixth power, inclusive, that are used in the Landau-Ginzburg-Devonshire thermodynamic potential for ferroelectric materials.

$SrTiO_3$ crystals (hereinafter referred to as — ST) are convenient for the investigation of flexoelectricity for a number of reasons. First, they have high dielectric susceptibility $\varepsilon = 310$ (1 kHz), second, they have a cubic symmetry $Pm\bar{3}m$ in a wide temperature range that doesn't mask the flexoelectric effect by piezoelectricity and, finally, the perovskite crystal structure is quite convenient for theoretical calculations. Experimental data shows that the permittivity at a temperature higher than 100 K follows the Curie-Weiss law $\varepsilon = C/(T - T_C)$, $T_C = 40$ K, decelerated growth of susceptibility is observed below this temperature and the crystal remains paraelectric up to 0 K due to the quantum effects and tetragonal distortion of the cubic structure below the antiferrodistortive structural transition 105 K [6–9]. In [10], it is shown that the dependence of permittivity on field in the temperature range of 90−230 K in the frequency range from 1 kHz to 1 MHz is adequately described by the following equation:

$$\varepsilon(T, E) = \frac{\varepsilon(T, 0)}{1 + \frac{A}{C} \varepsilon^3(T, 0) E^2}, \quad (4)$$

where $C = 8.5 \cdot 10^4$ K is the Curie constant, $A = 4.5 \cdot 10^{-18}$ K · m^2/V^2 is the constant for the [100] crystallographic direction independent of frequency and

temperature. The calculation shows that very strong fields shall be applied for considerable reduction of permittivity, which is confirmed by the findings of [11], according to which no permittivity variations are observed in a field up to 1 MV/cm. Only at a temperature below 65 K as the field increases, dielectric susceptibility decreases considerably starting from 10 V/cm [12,13].

Permittivity variation of ST crystals may also cause their uniaxial compression by very high pressure. Reduction of permittivity by $\sim 2\,\%$ at room temperature is observed at 1 kbar [14]. At low temperatures, uniaxial compression can cause ferroelectric phase transition and typical permittivity maximum. Thus, it is reported in [15] that spontaneous polarization appears and permittivity increases by an order of magnitude at the liquid helium temperature and critical stress of 10 kbar.

Dielectric response to inhomogeneous strain of ST crystals was investigated within the study of flexoelectricity. The first measurement of direct flexoelectric effect in ST single crystals was published in [16]. A 3 point bending method was used to provide vibrational bending of a $50-500\,\mu$m single-crystal wafer by a frequency of 30–40 Hz. Mechanical stress that causes the strain gradient of $0.1\,\mathrm{m}^{-1}$ at room temperature induced polarization of about 1 nC/cm. This corresponds to the transverse flexoelectric coefficient $\mu_{12} = 6.1 \cdot 10^{-9}$ C/m measured at low frequency. During cooling to 77 K, the induced polarization increased by an order of magnitude in the vicinity of the structural phase transition. At the approach to the ferroelastic transition of 105 K, anomaly was observed in the flexoelectric response, but was not detected in the permittivity at the same temperature. This anomaly was associated with the fact that the crystal was bended significantly at high static load, consequently, domain walls interacted with each other and, thus, their movement under this load was impossible. At low static forces, domain walls could move freely, while the strain gradient was maximum.

Investigation of the converse quasistatic flexoelectric effect effect also showed that, at a temperature above 110–120 K, the temperature dependence of ST wafer bending induced by the external homogeneous electric field is well described by the Curie-Weiss law [17]. In case of the converse effect, an anomaly was observed in the higher temperature range 110–120 K. Violation of direct proportionality of the flexoelectric response and permittivity in phase transition regions was also observed for ferroelectric ceramics [18].

This study addresses a dielectric response to a strain gradient to understand whether a linear approximation describing the direct flexoelectric effect in equations (1)–(3) is correct. If the inhomogeneous strain polarizes the crystal in the same way as the electric field, then can a nonlinear response be expected due to susceptibility variation under the action of this field? On the other hand, if the permittivity variation is a direct response to the strain gradient, then this phenomenon refers to uninvestigated effects and may be called flexodielectric similar to other flexoeffects: flexomagnetic, flexocaloric, etc.

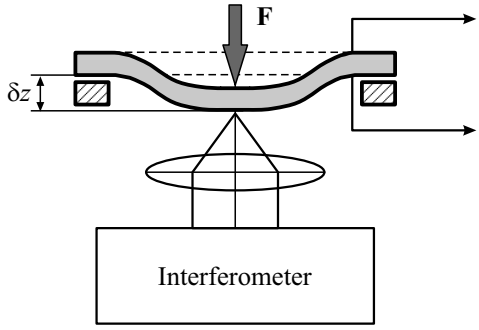

Figure 1. Direct flexoelectric effect test setup.

2. Experiment

This study investigated the direct flexoelectric effect using $140-150\,\mu$m $SrTiO_3$ thin wafers polished to the optic quality with a diameter of 10 mm and thermally sputtered mirror electrodes with a diameter of 6 mm. The wafer edges were secured to a fixed circular profile with a diameter of 9 mm. Spherical bending was performed by a needle-shaped sapphire probe with a tip $5\,\mu$m in diameter oriented to the center of the surface of the wafer (Figure 1). Inhomogeneous strain was induced by external mechanical load pulses with a low frequency (2–3 s) and an amplitude up to 1.5 N in the temperature range of 77–300 K. Wafer failure was observed at a load of 2 N. Wafer bending δZ was evaluated using a microscope-interferometer with a resolution up to 10 nm (the method is described in [19]). The induced polarization was calculated integration of current density measured using the U5-11 electrometric amplifier with a sensitivity of 10^{-15} A. Permittivity was measured using the E7-20 and GoodWill LCR-819 impedancemeters at 1 kHz. Relative permittivity measurement accuracy was 0.01 %.

3. Findings

Nonuniform mechanical load induces spherical bending strain of a ST thin wafer that in turn reduces the permittivity. It is convenient to write the permittivity variation as a relative value

$$\Delta\varepsilon/\varepsilon = (\varepsilon - \varepsilon_{\mathrm{F}})/\varepsilon,$$

where ε and ε_{F} are permittivities before and after loading, respectively. Figure 2 shows the linear dependence of $\Delta\varepsilon/\varepsilon$ on the strain gradient. The effect is sufficiently low, for example, the strain gradient equal to $0.5\,\mathrm{m}^{-1}$ causes a decrease in permittivity just by 0.04 %. As for the imaginary part of the complex dielectric polarization, any variations were limited to the sensitivity of a measuring system.

The same figure shows the linear dependence of the wafer polarization induced by spherical bending. Slope is equal to the effective longitudinal flexoelectric coefficient and is estimated as $\tilde{\mu}_{12} = 1.2\,\mu$C/m ($f_{1133} = 450$ V). The obtained values provide preliminary evaluation of so-called equivalent field that would induce polarization of the same magnitude

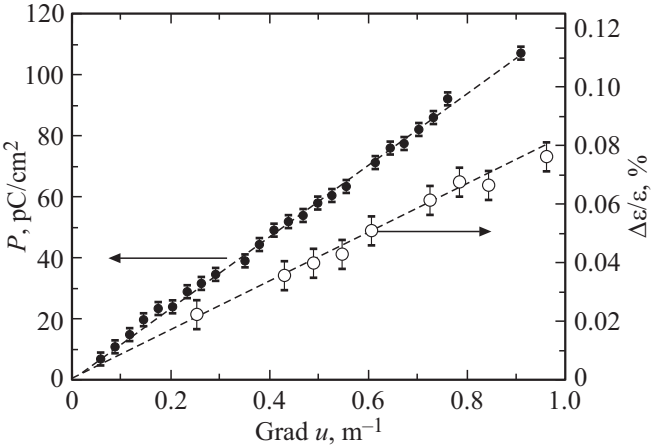

Figure 2. Dependence of the polarization (black circles) and permittivity variation (1 kHz) (white circles) on the strain gradient at room temperature.

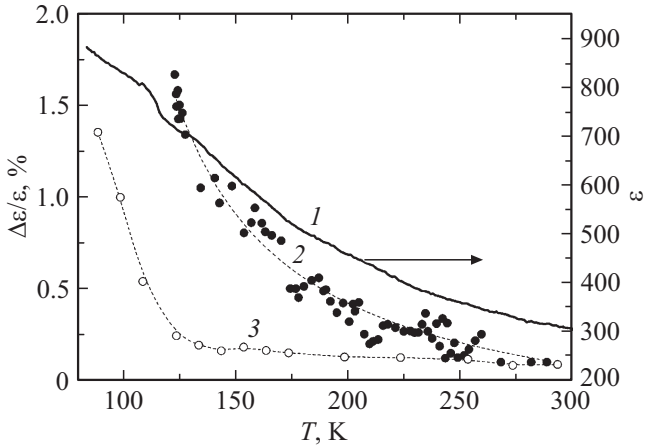

Figure 3. Temperature dependence: *1* — of permittivity (solid line), *2* — of relative permittivity variation with the strain gradient of $0.5\,m^{-1}$ (black circles) and *3* — permittivity variations in the 2.5 kV/cm field (white circles).

as the inhomogeneous strain effect. Thus, the strain gradient of $0.5\,m^{-1}$ induces polarization of $60\,pC/cm^2$. According to equation (2), the $E_{eq} = 20-25$ V/cm equivalent field would induce the same polarization magnitude. Note that this field strength is apparently insufficient to cause any significant permittivity variation in ST crystals in a deep paraelectric phase.

To check what external electric field strength induces the permittivity variation by 0.04 % of the same value as in the inhomogeneous strain of $0.5\,m^{-1}$, static voltage was applied to the wafer. It appeared that, in order to induce permittivity variation by 0.04 %, the $E = 2.5$ kV/cm field shall be applied, which is higher by two orders of magnitude than the equivalent field. Thus, in this case, the statement that the strain gradient, through the flexoelectric coupling, has the same effect as the external electric field is not quite correct.

To measure the inhomogeneous strain effect on permittivity in the temperature range of 120−300 K, mechanical load was used to cause the strain gradient with a fixed amplitude of $0.5\,m^{-1}$. As the temperature decreases from room temperature to the phase transition temperature of 110−120 K, the relative permittivity variation increases by an order of magnitude and reaches 1.5 % (Figure 3). The obtained temperature trend is adequately described by the following expression:

$$\Delta\varepsilon/\varepsilon \propto 1/(T - T_0)\ (T_0 = 70\,\mathrm{K}).$$

Note that the same dependence with the same $T_0 = 70$ K was obtained before for the field-induced inhomogeneous strain under the inverse flexoelectric effect [17]. The temperature dependence of $\Delta\varepsilon/\varepsilon$, when the external homogeneous field $E = 2.5$ kV/cm is applied, has another dependence (Figure 3). In this case, a growth of $\Delta\varepsilon/\varepsilon$ starts below 120 K. This situation demonstrates again the difference in permittivity variation mechanisms under the action of strain gradient and external electric field.

Conclusions

It was shown experimentally that the dependence of polar response on the strain gradient (direct flexoelectric effect) above the phase transition in thin ST wafers is adequately described by in a linear approximation. Nonlinearity of this effect associated with the dependence of susceptibility on inhomogeneous strain is quite low and is from fractions of one percent at room temperature to a value in the order of one percent at 120 K. Dielectric susceptibility variation is directly associated with the inhomogeneous strain effect in the crystal and differs from the electric field effect. This effect might be referred to as flexodielectric and, for its description, anharmonic terms of the standard thermodynamic Landau-Ginzburg-Devonshire potential for a ferroelectric material shall be included in the thermodynamic potential density equation for the flexoelectric effect.

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Conflict of interest

The authors declare no conflict of interest.

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