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Enhanced pyroelectric effect in self-supported films of BaTiO$_3$ with polycrystalline macrodomains

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Self-supported films of nanocrystalline BaTiO$_3$ exhibit a two orders of magnitude enhancement of the pyroelectric coefficient ($\approx 1 \mu C/cm^2 K$) with respect to the value measured for a single BaTiO$_3$ crystal. The enhancement strongly depends on film geometry and appears only in buckled films where ferroelectric grains undergo self-organization into polycrystalline macrodomains. The authors posit that the enhancement of the pyroelectric effect is related to $90^\circ$ polarization switching and is, therefore, similar in nature to an “extrinsic” piezoelectric effect. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730749]

It has recently been shown that in a buckled self-supported film of ferroelectric BaTiO$_3$ (Fig. 1), nanosized grains may reduce the intergrain stress by spontaneously forming zones within which the crystallographic directions of the grains become correlated. These zones, termed polycrystalline macrodomains, are similar to elastic domains in crystals but may contain hundreds or thousands of single-domain grains. In the buckled film, the nanosized grains self-organize into two types of macrodomains: (1) those with the $c$ axes of the grains aligned as close as possible to the direction perpendicular to the film (magenta regions in Fig. 1), henceforth “out-of-plane” macrodomains, and (2) those with the $c$ axes lying within the film plane (cyan regions in Fig. 1), henceforth “in-plane” macrodomains. The macrodomains self-assemble into linear (no curvature) and wedge-ordered (arc-shaped) regions (Fig. 1). Linear regions (no curvature) contain only out-of-plane macrodomains while wedge-ordered (arc-shaped) regions contain alternating triangular-shaped in-plane and out-of-plane macrodomains. The curvature radius of the wedge-ordered regions is equal to $R=D/t$, where $D$ is the film thickness and $t=c/a-1$ is the “tetragonality.” $a$ and $c$ are the crystallographic parameters of BaTiO$_3$ at a given temperature (Fig. 1).

Here we report that the pyroelectric coefficient of self-supported films of BaTiO$_3$ with polycrystalline macrodomains may be up to two orders of magnitude larger than that of a single BaTiO$_3$ crystal under similar conditions.

The pyroelectric coefficient was measured in nanocrystalline (30–80 nm) self-supported buckled films of BaTiO$_3$ with $D_{BTO}=750\pm100$ nm thickness and $W=200–250 \mu$m lateral dimensions [Figs. 1(a) and 1(b)], prepared as described in Ref. 1. The relative difference between the size of the film and the window constraining the film, henceforth the excess length $u_t=(L-W)/W$ [Fig. 1(a)], varied from 0% to 8%. The temperature of the tetragonal-to-cubic phase transition for all films was $>130^\circ C$, as detected by the complete disappearance of the birefringent regions and by the abrupt change in film shape. For the pyroelectric measurements, continuous bottom contacts and lithographically defined top contacts ($d_{Ag}=120\pm20$ nm Ag) were deposited by sputtering [Fig. 1(a)]. The polarization hysteresis loop could not be observed because fast switching of the polarization causes mechanical disintegration of the films. The films were poled by application of $\approx 3$ V electrical bias for 10–15 h. This value of the electrical bias was deliberately chosen since it is high enough to polarize the out-of-plane macrodomains, but it is not so high as to cause development of cracks and fissures.

A steplike periodic irradiation of the films with an infrared semiconductor laser [4,13] generates electrical current that only flows in response to switching the laser on and off [Fig. 2(a), inset]. This behavior persists unchanged for $>7$ days ($\approx 10^{11}$ cycles). The current was measured with a low impedance (<50 $\Omega$) amplifier (Fempta, Inc.). The phase of the pyroelectric current with respect to the heating/cooling cycle can be inverted by reversing the poling bias (supplementary material of Ref. 1). These facts uniquely identify the pyroelectric origin of the current and prove that the films were in the ferroelectric phase. The time dependence of the response to steplike heating or cooling followed an exponential decay law, $I(t)=I_0 \exp(-t/\tau)$ [Fig. 2(a)], from which the pyroelectric coefficient $\alpha$ was calculated. To measure the pyroelectric effect under conditions of mechanical clamping, the bottom contact of some of the films was covered with a 5–10 $\mu$m thick layer of pine resin. For this, the pine resin was dissolved in alcohol (5% w/v) and then applied to the back contact at a rate that permitted complete evaporation of the solvent. The thermal conductivity of the pine resin is $\approx 1000$ times lower than that of silver; therefore it does not significantly affect the temperature of the film during pyroelectric measurements.

The pyroelectric coefficient of films with excess length $4\% \geq u_t \geq 2\%$, measured as a function of temperature, has a clear maximum within the range of 20–80 $^\circ C$ [Fig. 2(b)]. In the vicinity of this maximum the pyroelectric coefficient reaches $\alpha=0.2–1 \mu C/cm^2 K$. This is up to two orders of magnitude larger than for single BaTiO$_3$ crystals. The pyroelectric current decay at 25 $^\circ C$ was fitted to an exponential $I(t)=I_0 \exp(-t/\tau)$. The time constant of the decay reached a limiting value $\tau=22\pm4$ s as $I(t)$ approached zero.
magnitude higher than that of a single crystal of BaTiO$_3$, at room temperature ($\varepsilon_{\text{cryst.25}} = 0.02 \, \mu\text{C}/\text{cm}^2\text{K}$). At temperatures above the maximum at 20–80 °C [Fig. 2(b)] the pyroelectric coefficient decays rapidly but shows another weak maximum at 120–140 °C, and above this temperature, vanishes completely [Fig. 2(b) inset]. The presence of the pine resin layer reduces the amplitude of the pyroelectric response in the vicinity of the first maximum by a factor of 20–100 but does not affect the magnitude of the pyroelectric effect in the vicinity of the second maximum. The layer of pine resin does not change the characteristic decay time, which indicates that the time-temperature profile of the samples remains unchanged.

The pyroelectric coefficient of films with $u_t < 2\%$ and $u_t > 4\%$ was found to be within the range of $(0.2–0.5) \times 10^{-2} \, \mu\text{C}/\text{cm}^2\text{K}$ and exhibited a single broad maximum at $-110 \, ^\circ\text{C}$ [similar to that shown in the inset of Fig 2(b)] when measured as a function of temperature. This is typical behavior for nanocrystalline ferroelectric ceramics and thin films of BaTiO$_3$. The presence of pine resin does not noticeably modify the pyroelectric behavior of these films.

The enhanced pyroelectric effect observed for films with $4\% > u_t > 2\%$ cannot be explained by any of the known contributions to pyroelectricity. Indeed, primary pyroelectricity, which is the change in spontaneous polarization with temperature in a mechanically unconstrained material in the absence of an electric field, is too weak to account for the magnitude of the pyroelectric current we observe. The secondary pyroelectric effect, which is related to the change in the dielectric constant with temperature, also cannot contribute significantly. This is so because the pyroelectric current was measured with a low impedance amplifier connecting the top and bottom contacts and the maximum potential difference between the contacts could not exceed $U_s = (20 \, \text{nA}) \times (50 \, \Omega) = 1 \, \mu\text{V}$ (20 nA is the maximum registered peak current). Therefore, the contribution to the pyroelectric coefficient that can be induced by the potential difference is $(U_s \varepsilon_0 \varepsilon)/(d\varepsilon/d\Theta)$, where $\varepsilon_0$ is the dielectric permittivity of vacuum and $\varepsilon$ is the dielectric constant of the film. One can see that even for very large values of $(d\varepsilon/d\Theta)$, for example, in a polymeric material, the contribution to the pyroelectric effect is negligibly small, on the order of $10^{-6} \, \mu\text{C}/\text{cm}^2\text{K}$.

A stress-induced contribution to the pyroelectric current may arise only from the stress associated with thermal expansion because no external forces act on the self-supported film. The distributions of stress and strain in a film buckled with $C_{4v}$ symmetry [see Fig. 1(b)] are complex. However, the thermally induced stress in a buckled film is always smaller than that in a flat clamped film of the same dimensions.

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3E. H. Putley, The Pyroelectric Detector, in Semiconductors and Semimetals, Chap. 6, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1970), Vol. 5, p. 259–285. The film can be viewed as a square membrane, the edges of which are kept at constant temperature. Then the pyroelectric coefficient is given by
\[ \frac{I}{4} = \frac{CA}{Pd^2} \]
where
\[ CA = \frac{D_{BTO} C_{BTO}}{C_{BTO} + 2d_A C_{Ag}} \]
are the thermal capacitances of the film and the contacts, respectively. The applicability of the method was verified by comparing the measured characteristic decay time \( \tau \) with the time predicted by the model, \( \tau = \frac{W^2}{2(\pi^2 \gamma_A)} \), where \( \gamma_A = \left( D_{BTO} \lambda_{BTO} + 2d_A \lambda_{Ag} \right) / C_A \) is the lateral thermal diffusion coefficient of the film with contacts, \( \lambda_{BTO} \) and \( \lambda_{Ag} \) are the thermal conductivities of the film and the contacts, respectively. For the case under consideration, the calculated and observed times agree to within 15%.