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FLEXOELECTRICITY IN ANTIFERROELECTRICS

P. Vales-Castro[1], Krystian Roleder[2], Lei Zhao[3], Jing-Feng Li[3], Dariusz Kajewski[2], Gustau Catalan[1,4]

[1] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus Universitat Autonoma de Barcelona, Bellaterra 08193, Spain; email: pablo.vales@icn2.cat

[2] Institute of Physics, University of Silesia in Katowice, ul. Uniwersytecka 4, 40-00 Katowice, Poland.

[3] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

[4] Institut Català de Recerca i Estudis Avanc¸ats (ICREA), Barcelona 08010, Catalonia; email: gustau.catalan@icn2.cat

ABSTRACT

Flexoelectricity (coupling between polarization and strain gradients) is a property of all dielectric materials that has been theoretically known for decades, but only relatively recently has it begun to attract experimental attention. As a consequence, there are still entire families of materials whose flexoelectric performance is unknown. Such is the case of antiferroelectrics: materials with an antiparallel but switchable arrangement of dipoles. These materials are expected to be flexoelectrically relevant because it has been hypothesised that flexoelectricity could be linked the origin of their antiferroelectricity. In this work, we have measured the flexoelectricity of two different antiferroelectrics ($PbZrO_3$ and $AgNbO_3$) as a function of temperature, up to and beyond their Curie temperature. Although their flexocoupling shows a sharp peak at the antiferroelectric phase transition, neither flexoelectricity nor the flexocoupling coefficients are anomalously high, suggesting that it is unlikely that flexoelectricity causes antiferroelectricity.

Antiferroelectricity was first proposed by Kittel in 1951 in a theory based on antiparallel dipolar displacements analogous to antiferromagnetism [1], and it was experimentally reported at the end of the same year [2] . Compared to their ferroelectric counterparts, however, antiferroelectrics have been less researched, partly due to their relative rarity, but also because, not being polar, their practical applications are less obvious. So far, they have been studied mostly in the context of electrostatic energy storage [3], [4], but also in electrocaloric applications thanks to their anomalous (negative) effect [5], [6], and for high-strain actuators [7], [8]. Recently, a record-breaking photovoltaic field (6MV/cm, the highest ever measured for any material) has also been reported in $PbZrO_3$, opening a new line for antiferroelectrics in photovoltaic applications [9].

Owing to their centrosymmetric ground state, antiferroelectrics (AFEs) are not suitable for direct piezoelectric transduction (conversion of strain into voltage). They can, however, be flexoelectric (conversion of strain gradient into voltage). This effect is allowed by all crystal symmetries [10] and it is the result of a linear coupling between a strain gradient and polarization that follows the equation:

$$P_i = \mu_{klij} \frac{\partial u_{kl}}{\partial x_j} \tag{1}$$

Mashkevich & Tolpygo [11], [12] were the first ones to propose such an effect, and Kogan [13] later developed the phenomenological theory. Although it was initially predicted that flexoelectricity would be low in simple dielectrics ($\mu \approx 10^{-10}$ C/m), its proportionality to the permittivity [14], [15] meant that it could reach much higher values, of the order of nC/m and even μC/m in ferroelectrics and relaxors [16]. Moreover, thanks to barrier-layer effects, even bigger effective coefficients (mC/m) can be reached in semiconductors [17]. In addition, flexoelectricity has become a growing field in the last decade with the development of nanoscience, thanks to the inverse proportionality between a device's size and the strain gradients that it can withstand [18].

In the case of AFEs, there is specific interest in their flexoelectricity because it was theoretically predicted by Tagantsev *et al.* [19] and also discussed by Borisevich *et al*. [20] that flexoelectric coupling could be responsible for stabilizing the AFE phase. The idea behind such theories is that antiferroelectric ordering can be viewed as a form of extreme polarization gradient, since polarization alternates every half unit cell (Figure 1a). The existence of strongly localized electric field gradients at the cationic sites of the antiferroelectric lattice is consistent with first principles calculations [21]. The implicit hypothesis is that such spontaneous "polarization gradients" (antipolar arrangements) could be caused by an anomalously strong flexocoupling contribution to the lattice mode responsible for the paraelectric to antiferroelectric phase transition [22]. It is the purpose of this paper to examine whether antiferroelectrics display anomalous flexoelectricity by measuring the flexoelectric and flexocoupling coefficients of the archetype AFE material, $PbZrO_3$, and also of pure $AgNbO_3$, a lead-free AFE. [1]

Fabrication details and antiferroelectric loops of the ceramic $PbZrO_3$ and $AgNbO_3$ samples are provided in refs. [23] and [3], respectively. Scanning electron microscopy examination of the samples (not shown) shows that the average grain size for the $PbZrO_3$ ceramic is 4 microns while the latter has an average grain size of 5 microns. Their flexoelectricity has been measured by the method developed by Zubko et al. [24]: a dynamic mechanical analyzer (DMA 8000, Perkin-Elmer) is used to apply a periodic three-point bending stress whilst simultaneously recording the elastic response (storage modulus and elastic loss). The DMA's mechanical force signal is fed into the reference channel of a lock-in amplifier

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[1] Although in $AgNbO_3$, a weak ferroelectric-like polarisation of the order of $4x10^{-4}$ C/m^2 has been reported [37], this residual polarization is thought to be metastable, with the ground state being antiferroelectric [38].

(Stanford Research Instruments, model 830), while the samples' electrodes are connected to the measurement channel of the lock-in amplifier, which records the bending-induced displacement currents. The displacement current is converted into polarization using $P_i = I/2\pi\nu A$, where ν is the frequency of the applied force (13 Hz in our experiments) and A is the area of the electrodes. The polarization measured by the lock-in is related to the effective flexoelectric coefficient μ_{13}^{eff}:

$$\bar{P}_3 = \mu_{13}^{eff}\,\overline{\frac{\partial u_{11}}{\partial x_3}} \tag{2}$$

$$\overline{\frac{\partial u_{11}}{\partial x_3}} = \frac{12z_0}{L^3}(L-a) \tag{3}$$

where L is the separation between the standing points of the ceramic, *a* is the half-length of the electrodes, and z_0 is the displacement applied in the middle of the sample. The mechanical, flexoelectric and dielectric properties were recorded first at room temperature and then as a function of temperature up to 250 °C for the $PbZrO_3$ and 400 °C for the $AgNbO_3$. For temperature measurements a Perkin-Elmer cover is used to enclose the three-point bending system. It has a system of hot resistances and it is also connected to a source of liquid nitrogen. A thermocouple is placed close to the sample for accurate temperature measurements. The temperature is controlled by means of a feedback loop monitored by the DMA software, with ramps of 3 °C/min in both cases.

The electrodes' lengths were, in all cases, longer than the distance between the loading pins. Therefore, the length ratio d/L (where d=length of sample, L=distance between loading edges) was delimited by the size of the sample with respect to the loading pins, which was in all cases larger than 1, with the largest being 1.14.

Four and six sets of samples were measured for $PbZrO_3$ and $AgNbO_3$, respectively. For every sample, at least three different displacements (strain gradients) were applied, each of them done a minimum of two times measured at 13 Hz for 15 minutes each, which translates into 11700 flexoelectric measurements for every run of strain gradient.

A representative example of room-temperature flexoelectricity is shown in Figure (2), where the slope of the linear fit to the data using eq. (2) represents the flexoelectric coefficient. The average room-temperature flexoelectric coefficients for all the measured sets are 3.9 ± 0.2 nC/m and 3.8 ± 0.5 nC/m for $PbZrO_3$ and $AgNbO_3$, respectively. These room-temperature flexoelectric coefficients are not particularly large; they are considerably smaller than reported for ferroelectrics and relaxors [16], and comparable to the flexoelectricity of $SrTiO_3$ [24], a non-polar perovskite.

We also calculated the flexocoupling coefficient (flexoelectricity divided by dielectric permittivity), obtaining average values of 5.1 ± 0.3 V and 2.9 ± 0.4 V for $PbZrO_3$ and $AgNbO_3$, respectively. These values are inside the standard range (1-10 V) predicted [13], [25] and measured [26] for non-antiferroelectric materials, thus not showing the enhancement that might have been expected if antiferroelectricity is driven by flexoelectricity.

On the other hand, room temperature is far below the antiferroelectric phase transition temperature of these materials. If flexoelectricity truly has an influence on antiferroelectricity, such coupling should manifest itself most strongly at the phase transition. We therefore characterized the two antiferroelectrics also as a function of temperature across their phase transitions. The temperature-dependent measurements were difficult to repeat across the full temperature range, as the structural transition often caused samples to break. The results shown are those that gave the most stable signal across the largest temperature range.

The dielectric and mechanical properties are shown in Figure (3), and the flexoelectric and flexocoupling coefficients are shown in Figure (4). Lead zirconate displays a simple Curie-Weiss behaviour as a function of temperature, with a permittivity peak at the critical temperature (T_C=225 ^oC) of the antiferroelectric-to-paraelectric phase transition. Concomitant with this peak, there is an abrupt change (a softening) of the mechanical properties and a maximum in the flexoelectric coefficient, μ_{13}^{eff}. The *flexocoupling* coefficient as a function of temperature, f_{13}^{eff}, shown in Figure (4a), stays remarkably constant around 2-3V until, about 50 degrees below T_C, it starts to rise, reaching a peak value of 22 V at the transition. Just above the transition, the flexocoupling sharply drops to a value smaller than 1V.

Silver niobate is somewhat more complex, because it has several structural transitions [27], [28] before the antiferroelectric-paraelectric phase transition at 350°C. These phase transitions have a noticeable impact on the flexoelectric coefficient, which shows discontinuities at each of these phase changes, before rising from few nC/m at room temperature to tens of nC/m at the antiferroelectric Curie temperature. The effective flexoelectric coefficient of $AgNbO_3$ continues to rise beyond the Curie temperature, but the dielectric losses also shoot up, suggesting that the high-temperature enhancement in effective flexoelectricity may be due to a semiconductor mechanism [17]. Like the flexoelectric coefficient, the flexocoupling coefficient of $AgNbO_3$ as a function of temperature (Figure (4d)) also shows anomalies at all the phase transitions, but in all cases it stays within the moderate range predicted for simple dielectrics ($f < 10$ V). The flexoelectriticy of AFE ceramics is therefore not anomalously high.

One possible objection to these experimental results is that, below T_c, $PbZrO_3$ and $AgNbO_3$ are ferroelastic, and therefore twinning might in principle accommodate part of the induced strain gradient, thus reducing the apparent flexoelectric coefficient (as has been observed also in $SrTiO_3$ below its ferroelastic phase transition [24]). However, above T_c there is no ferroelasticity, and yet the measured flexocoupling coefficient still remains low. Ferroelastic relaxation of strain gradient is therefore not the cause of the low effective flexoelectricity. Another question concerns the role of surface piezoelectricity, particularly in a ceramic in which grain boundaries provide additional surfaces. However, for the few materials for which we can compare single crystals and ceramics [26], grain boundaries appear to increase, rather than decrease, the effective flexoelectricity. Moreover, octahedral rotations in the lattice [29], [30] nanopolar regions, self-polarization or processing-induced strain gradients [31] have all been shown to also increase the flexoelectric coefficient, and in spite of these potential contributions the results for antiferroelectrics remain low. The conclusion thus remains that the experimentally measured flexoelectricity of antiferroelectrics is not inherently high. Similar perovskite oxides, such as $SrTiO_3$, have even higher flexoelectric coefficients and do not develop antiferroelectricity, so it is hard to argue that antiferroelectricity is caused by flexoelectricity –at any rate, it is not caused by an anomalously large flexocoupling. This result will have to be taken into account by any future theory of the interplay between flexoelectricity and antiferroelectricity [19], [20].

On the other hand, after dividing the flexoelectric coefficient by the permittivity, the resulting flexocoupling coefficient f is expected to be constant for ordinary materials, because the temperature dependence is mostly contained in the permittivity. In contrast, however, the flexocoupling coefficients of our antiferroelectrics increase sharply near the antiferroelectric phase transition. While their magnitude still remains within the theoretically acceptable range, this sharp peak in flexocoupling near T_C is unexplained. In $PbZrO_3$, perhaps part of this increase in effective flexoelectricity can be attributed to the appearance of an intermediate polar phase reported to exist for a few degrees right under the transition [32] at an energy of only 4 cal/mol away from the antiferroelectric state [33], and linked to local strains due to defects in lead and oxygen sublattices [34] combined with strongly anharmonic optic–acoustic mode coupling [35]. However, the observed temperature range of stability of this polar phase [36] is narrower than the width of the observed peak in flexoelectricity. In addition, while polar regions may perhaps contribute to the flexoelectric enhancement of $PbZrO_3$, $AgNbO_3$ remains strictly non-polar in temperatures above 75°C, so its flexoelectric peak cannot be associated with parasitic piezoelelectricity. The possible involvement of flexoelectricity in antiferroelectricity thus appears to be non-trivial: the coupling is low both in the paraelectric and the antiferroelectric phases, but the presence of a sharp flexocoupling peak at the critical point of the antiferroelectric transitiondeserves further scrutiny.

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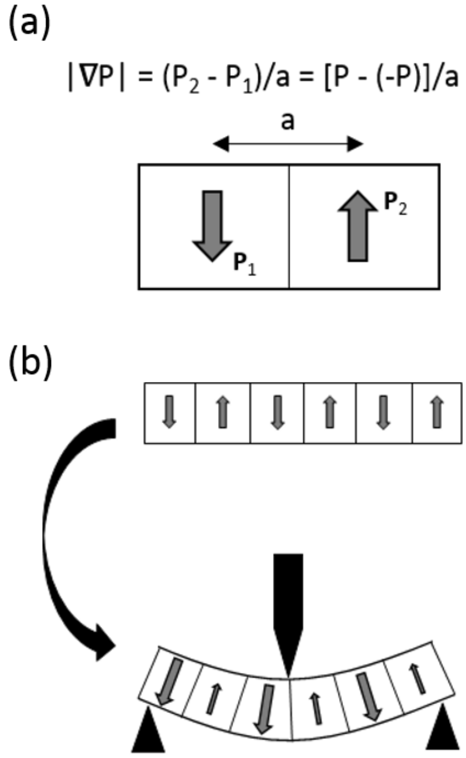

***Figure 1** (a) Visualizacion of antipolar arrangement as a form of polarization gradient, where P is the sublattice polarization and a is half the length of the antiferroelectric unit cell, and (b) schematics of how antipolar polarization is expected to respond as a strain gradient is applied*

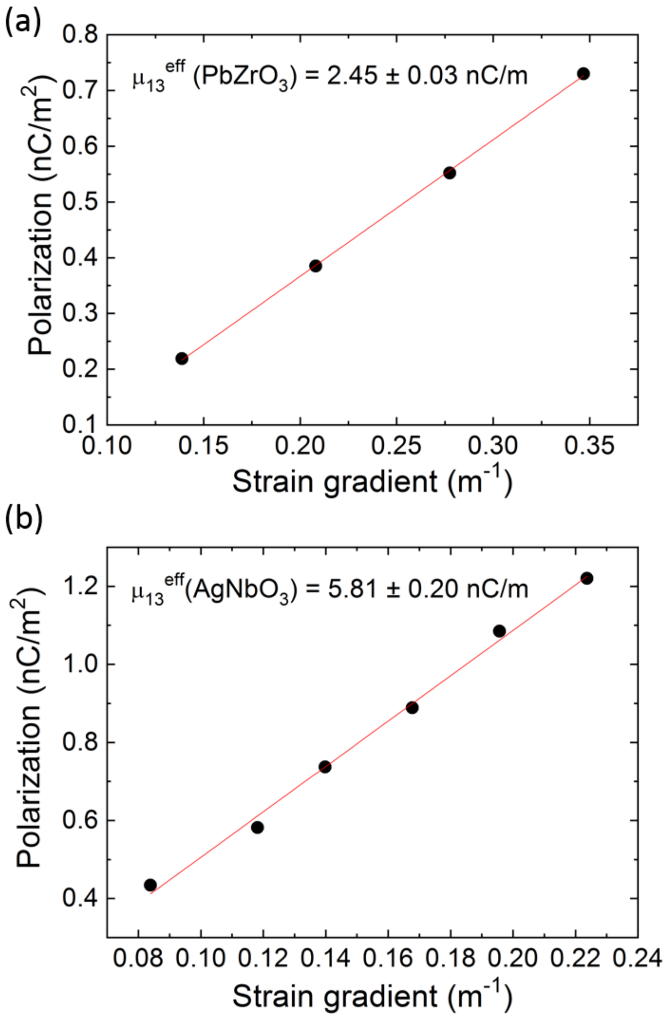

Figure 2 Measurement of the flexoelectric coefficients of (a) $PbZrO_3$ and (b) $AgNbO_3$ at room temperature. The flexoelectric coefficient is calculated as the slope of the linear fit to the polarization vs strain gradient.

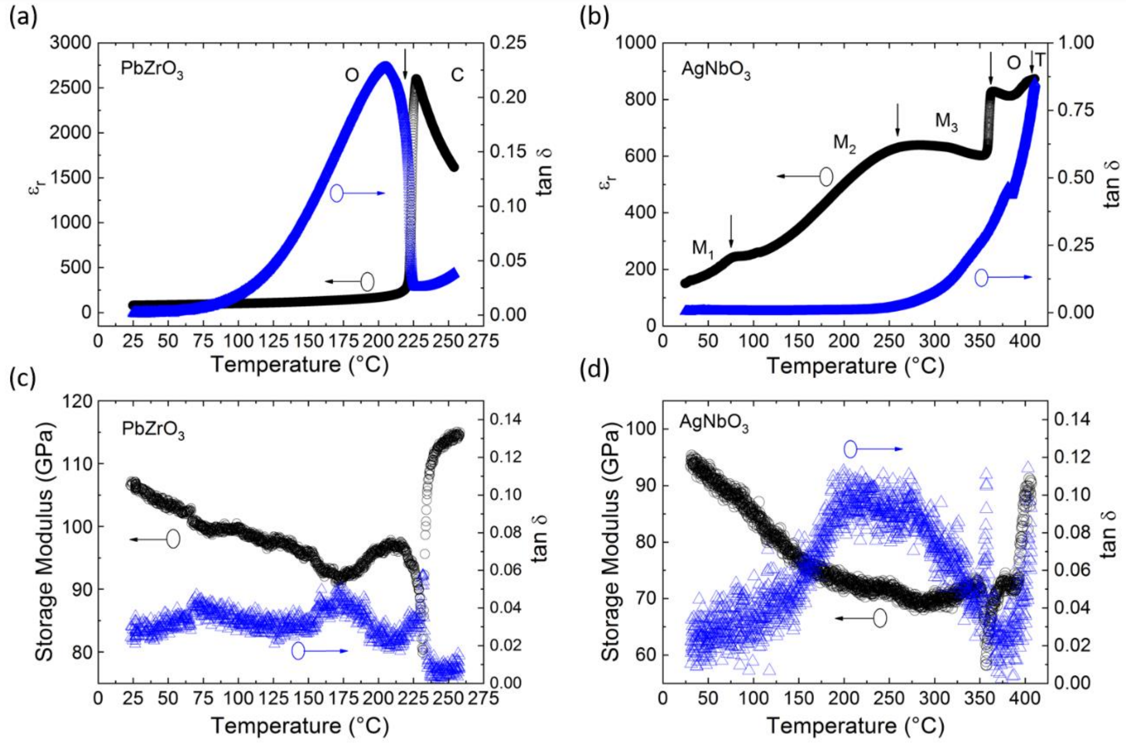

Figure 4 Relative permittivity and mechanical properties of (a), (c) $PbZrO_3$ and (b), (d) $AgNbO_3$ with their respective phase changes: M (monoclinic), O (orthorhombic), T (tetragonal) and C (cubic).

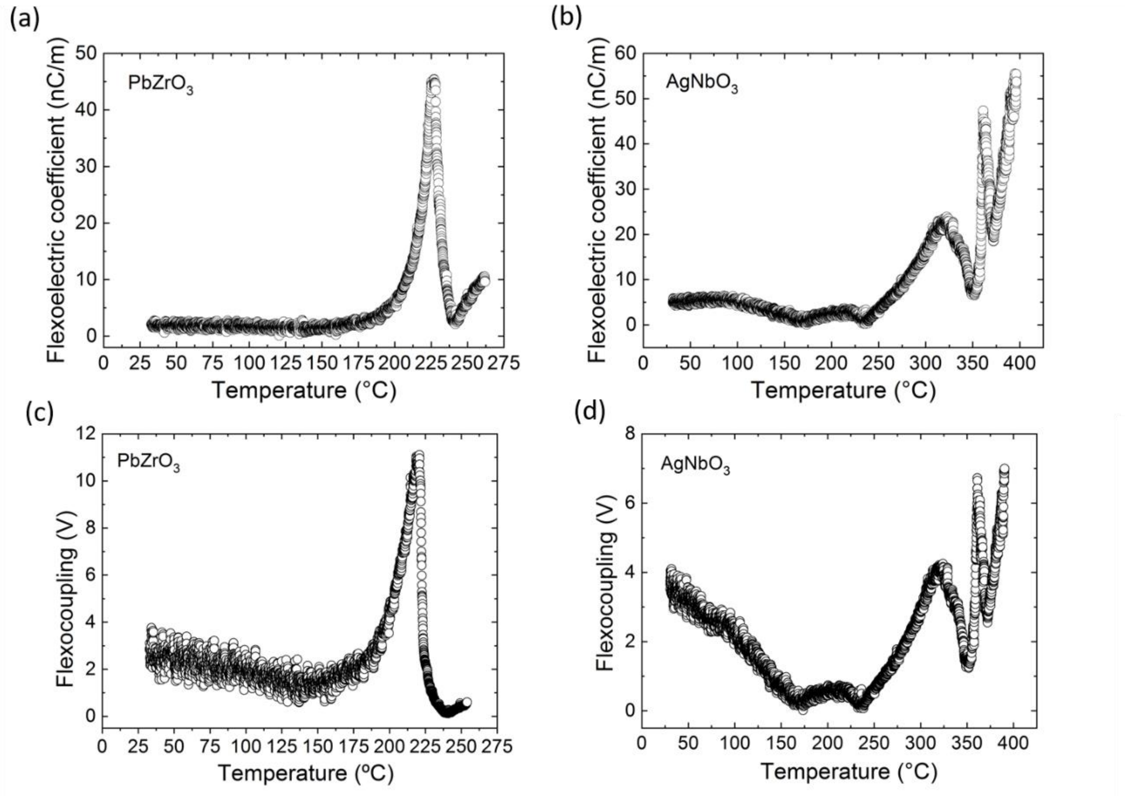

Figure 3 Flexoelectric coefficient and flexocoupling for (a), (c) $PbZrO_3$ and (b), (d) $AgNbO_3$ up to and beyond their antiferroelectric-to-paraelectric phase transition as a function of temperature