

Huge low-temperature polarity in the antiferroelectric PbHfO_3

Krystian Roleder¹, Andrzej Majchrowski², Jan K. Zaręba³, Annette Bussmann-Holder⁴, Iwona Lazar^{1,*}

Irena Jankowska-Sumara⁵, Dariusz Kajewski¹, and Andrzej Soszyński¹

¹*Institute of Physics, University of Silesia in Katowice, ul. 75 Pułku Piechoty 1, 41-500 Chorzów, Poland*

²*Institute of Applied Physics, Military University of Technology, ul. Kaliskiego 2, 00-908 Warsaw, Poland*

³*Institute of Advanced Materials, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

⁴*Max-Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

⁵*Department of Exact and Natural Sciences, University of the National Education Commission, Podchorążych 2, 30-084 Kraków, Poland*



(Received 12 February 2025; revised 24 April 2025; accepted 7 May 2025; published 16 June 2025)

Another polar phase was discovered in lead hafnate PbHfO_3 single crystal below 270 K. The transition was manifested through complex permittivity anomalies with a thermal hysteresis of approximately 30 K. While pristine PbHfO_3 crystal was shown to have modest pyroelectric signals of 20–235 nC cm⁻², DC field poling at 10 kV cm⁻¹ induced a huge polarization of 60 μC cm⁻², dramatically larger than values observed in lead zirconate PbZrO_3 . The polar nature of this transition was validated through multiple experimental techniques. Similarly to dielectric measurements, the pyroelectric effect showed distinct thermal behavior between cooling and heating cycles. The distinct change in the polarization gap occurring in the polarization–electric field function was observed below the transition. Second harmonic generation measurements have displayed signals sensitive to applied DC fields around the transition point. It was suggested that the mechanism behind this polar transition involves complex interactions within both Pb^{2+} and O^{2-} substructures. The possible symmetry of this low-temperature polar phase was considered based on the absence of the piezoelectric coefficients d_{31} and d_{33} .

DOI: [10.1103/ftn5-cx2n](https://doi.org/10.1103/ftn5-cx2n)

I. INTRODUCTION

The structural intricacies of antiferroelectric materials, particularly those of oxygen perovskites ABO_3 , continue to challenge our understanding of their fundamental nature. According to Kittel [1], an antiferroelectric compound is like a ferroelectric one since its structure is obtained through distortions of a nonpolar high-symmetry reference phase. The distortion is polar for ferroelectrics, while there are local substructures of polar distortions for antiferroelectrics, the sum of which yields a net zero polarization. Although the occurrence of an antiferroelectric state in the structure of the ABO_3 perovskite is observed experimentally, there are increasing doubts as to whether it exists in stoichiometric systems since the antiferroelectric phase contains domains but also exhibits ferroelastic properties. These appear with polar domain boundaries, polar phase transition, weak polarity at low temperatures (<270 K), and rarely studied dipole glass state properties below 10 K [2–5]. The PbHfO_3 (PH), like an isostructural compound PbZrO_3 (PZ), shows a wealth of physical phenomena. In lead zirconate, above the transition point at $T_c = 490$ K to the paraelectric state, fluctuating symmetry breaking and static micropolarity are

observed, separated by—theoretically predicted and experimentally confirmed—temperature limit $T_{\text{BH}} = 1.1 T_c$ [6]. Its occurrence was confirmed by the local disorder of oxygen octahedra observed in neutron scattering [7]. Below T_c , in the nominally antiferroelectric phase, polar interdomain boundaries (with ferroelectric ordering) and weak polarity occur below 270 K [5]. PZ's antiferroelectric phase transition mechanisms were studied intensively using various experimental methods, e.g., Refs. [4–9]. Studies on the lattice dynamics of these crystals revealed the important role of the interplay between the zone-center ferroelectric mode and the zone-boundary antiferroelectric mode or multiple softening lattice modes over the whole Brillouin zone [10,11].

For the PH crystal, the observed phenomena above $T_c = 476$ K are similar to those of PZ, but the structural properties differ distinctly below T_c . Although the low-temperature antiferroelectric phase (AFE1) of PH is isostructural with the orthorhombic $Pbam$ phase of PZ [12,13], unlike PZ, an intermediate (second) antiferroelectric phase (AFE2), between 433 and 476 K, occurs. The paper by Huband [14] suggests that the intermediate phase is consistent with orthorhombic symmetry in rhombic orientation. More recently, an inelastic x-ray scattering (IXS) study in PH [15], covering the lattice dynamics in the cubic phase and intermediate AFE2, established that the intermediate AFE2 phase under ambient pressure is characterized by a long-wavelength modulation in the lead substructure, with modulation wave vector $q = (0.15, 0.15, 0)$ in pseudocubic coordinates, and antiphase rotations of the oxygen octahedral suggesting that the AFE2 phase is incommensurate (IC), driven by the antiferrodistortive (AFD) soft mode containing two distortions.

*Contact author: iwona.lazar@us.edu.pl

One is related to Pb^{2+} cation displacement ordering, and the other to octahedral tilts—which arise simultaneously at the phase transition. On the other hand, these two distortions may be separated under hydrostatic pressure [16]. Although Bosak *et al.* [17] made a structural analysis of the incommensurate phase and proposed the symmetry of this phase as orthorhombic with $Imma(00\gamma)s00$ superspace group, the formation mechanism of such an intermediate phase remains unknown.

The literature data mainly concern the high-temperature properties of PH. Our experiments described below deal with dielectric properties of PH at low temperatures. We have found that the PH is polar below 269 K. Surprisingly, low-temperature polarization takes huge tens of $\mu\text{C cm}^{-2}$ values after poling in the DC field.

II. METHOD

A. Crystal growth

The incongruently melting PH crystals were grown in the following way: The solvent we used to lower the crystallization temperature below the point of peritectic transition was lead oxide, the so-called self-flux that does not introduce additional ions into the melt. Instead of PbO , Pb_3O_4 was used as a source of Pb^{2+} ions. The presence of Pb^{4+} ions improves oxidizing conditions, and as-grown PH single crystals have much better optical quality than those grown from PbO solvent. Though pure Pb_3O_4 decomposes around 500°C , mixing different chemical compounds in the melt probably allows the formation of some intermediate compounds containing Pb^{4+} ions and improves the quality of growing crystals. It was found that the addition of B_2O_3 ($\text{PbO}:\text{B}_2\text{O}_3$ molar ratio 4:1) also has a beneficial influence on crystallization conditions. It diminishes the volatility of PbO and lowers the possible temperature of crystallization down to 700°C . Growth of PH was carried out through spontaneous crystallization, and the growing crystals were submerged in the melt. This way, avoiding the loss of PbO from as-grown crystals was possible. Owing to the low solidification temperature of the flux, the decantation of as-grown crystals was carried out at temperatures securing their compositional stability.

The crystallization was carried out in a platinum crucible covered with a platinum lid under conditions of a low-temperature gradient. After soaking at 1473 K for 24 h, the melt was cooled to 1150 K at a rate of 2.5 K h^{-1} , and after decantation, the furnace was cooled to room temperature at a rate of 10 K h^{-1} . As-grown PH single crystals were etched in hot diluted acetic acid to remove residues of the solidified flux.

Energy-dispersive x-ray spectroscopy (EDS) was used to investigate the chemical composition of the obtained crystals. The content of Pb^{2+} and Hf^{4+} ions expressed in atomic percentage was homogeneous in the whole crystal and equaled 51.8/48.2, while it should be 50/50. Considering the EDS method's error estimated at $\pm 1\%$, one can say that the crystal, within the limits of experimental error, was close to stoichiometric composition in the Pb and Hf substructures.

B. Dielectric and pyroelectric properties

Dielectric and pyroelectric experiments were performed on PH single crystals with sizes of $3.375\text{ mm} \times 2.125\text{ mm} \times 0.4\text{ mm}$ (thickness). Silver paste electrodes were used to measure capacity and conductance at frequency 1 MHz using an Agilent 4192 A impedance analyzer on a heating/cooling rate of 1 K min^{-1} . The sample was held by the Linkam THMS600E temperature stage, which maintains a constant temperature of 0.1 K. The real ϵ' and imaginary ϵ'' part of permittivity were calculated knowing the sample geometry.

C. Polarization gap measurements

The polarization P_r dependence due to an electric field pulse E_3 employed the Multiferroic II Ferroelectric Radiant Tester (index 3 for the electric field means in the pseudocubic $[001]_c$ direction). First, a hysteresis test had a preset loop with the sine signal of a frequency of 1 Hz and an electric field of 10 kV cm^{-1} . After a delay of 1 s, the next loop measurement was carried out at the same field and frequency. For such a pulse procedure, a gap in the $P_r(E_3)$ run occurs, provided there is a polar state of decay inside the crystal.

D. Second harmonic generation (SHG)

Investigations were conducted on another PH single crystal from the same technological process, with the size of nearly a cube of $1.5\text{ mm} \times 1.5\text{ mm} \times 1.2\text{ mm}$ (thickness). Its dimensions allowed electrodes to be put on the sample to apply an electric field and have a surface of enough dimensions to accommodate a laser beam. The laser fluence at samples was equal to 0.46 mJ cm^{-2} . The crystal was placed in the Linkam LTS420 stage with stability equal to $\pm 0.1\text{ K}$, and the setup operated in the reflection mode. Specifically, the laser beam from the regenerative amplifier was directed onto the crystal's plane (001) at 45° . The emission collecting optics consisted of a diameter 25.0 mm planoconvex lens with a focal length of 25.4 mm, mounted to the 400- μm 0.22 NA glass optical fiber and placed along the normal to the sample surface. The distance between the collection lens and the sample was 30 mm. The spectra of the nonlinear optical (NLO) responses were recorded by an Ocean Optics Flame T fibre-coupled charge-coupled device spectrograph with a 200- μm entrance slit. Scattered pumping radiation was suppressed using a Thorlabs 750-nm short-pass dielectric filter (FESH0750).

III. RESULTS AND DISCUSSION

The temperature dependence of the anisotropic permittivity ϵ'_{33} and dielectric losses ϵ''_{33} at a frequency of 1 MHz for a PH single crystal are presented in Fig. 1(a). Between 230 and 270 K, a distinct anomaly in $\epsilon'_{33}(T)$ and the $\epsilon''_{33}(T)$ runs is characteristic of a possible transition point. The two diffused maxima on the $\epsilon''_{33}(T)$ may testify about somewhat complex properties when approaching the transition point. The dependencies on cooling and heating were similar but shifted relative to each other by about 30 K towards lower temperatures.

Distinct changes of the pyroelectric current $I_p(T)$ detected on cooling and heating for the pristine single-domain crystal with silver electrodes on surfaces perpendicular to $[001]_c$

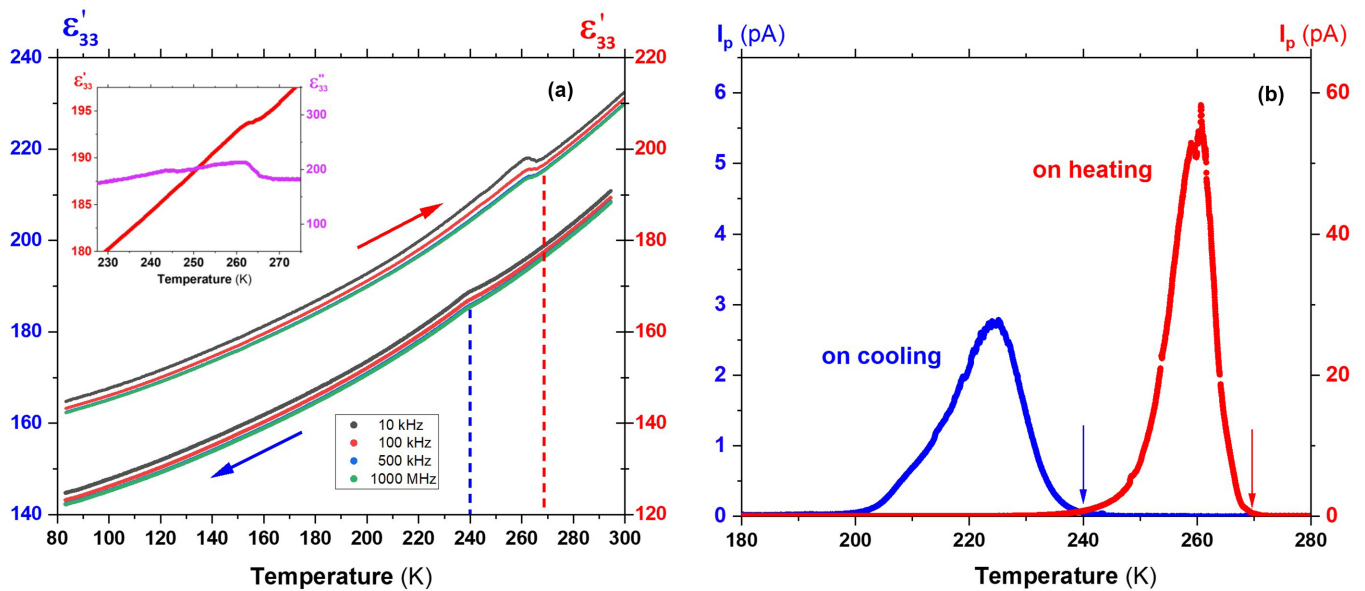


FIG. 1. (a) Temperature dependence of the real ϵ'_{33} part of the permittivity for a single domain PH crystal in the $[001]_c$ pseudocubic direction, measured at a few frequencies, on cooling and heating, showing distinct thermal hysteresis. Inset in (a) shows a transition point near 270 K accompanied by anomalies in the real and imaginary parts of permittivities for 1 MHz. (b) The temperature dependence of the total pyroelectric current I_p on cooling and heating shows a similar distinct thermal hysteresis, as in the case of the permittivity. Note that on cooling, the y-axis values are ten times smaller. After integrating the dependence of I_p as a function of time, polarization changes of the order of 20 nC cm^{-2} (on cooling) and 235 nC/cm^{-2} (on heating) have been obtained.

pseudocubic axis are presented in Fig. 1(b). The data are typical for a transition to a polar phase. What is interesting is the big difference between changes in polarization calculated from the pyroelectric measurements on cooling and heating. Because the changes on heating are ten times bigger, the transition looks highly diffused and probably needs time to be established at low temperatures.

However, after poling the same crystal under the DC field of 10 kV cm^{-1} and cooling from 300 to 83 K, the value of polarization decaying at the transition point and calculated from the pyroelectric current amounted to a huge value of $60 \mu\text{C cm}^{-2}$ (Fig. 2). This huge and saturated polarization was reproducible after subsequent poling processes. The detection of the pyroelectric current on heating [Fig. 2(c)] started after 2 h of switching off the poling DC at 83 K. The depolarizing current at 83 K is shown in Fig. 2(a), and the polarization accompanied by this depolarization was estimated to be $0.5 \mu\text{C cm}^{-2}$ only. These results point to a stable polar state in the PH crystal. It also has to be stressed that poling conducted under the same conditions, however, in the opposite DC field causes the reversal of the pyroelectric current, which proves that the low-temperature polar phase in the PH crystal is of ferroelectriclike nature.

To test the low-temperature polarity in the PH crystal, we have investigated changes in the polarization gap $P_r(E_3)$ (Fig. 3). The origin of this gap can be attributed to various mechanisms, including mobile free charge, space charge from carriers, piezoelectric energy storage, heat dissipation, charge traps at the electrode interfaces, or depletion region modulation. Investigating this gap in the case of antiferroelectric PH with centrosymmetric symmetry may test its polarity, if any, because all the above-mentioned mechanisms can be

neglected in the PH crystal, being antiferroelectric and highly insulating.

The character of the dependencies presented in Fig. 4 raises a question of whether the signals originated from a bulk transition between two intrinsically stable phases of polar and antipolar order or are associated with defects like skin layers, dislocations, or vacancies. Given that the antiferroelectric phase of $Pbam$ symmetry is centrosymmetric, we should not observe any SHG response. However, it exists below the observed transition.

Interestingly, the SHG signal is very clear in the phase below 270 K and is sensitive to the DC field action, which makes this signal stronger. It shows that the SHG is only sensitive to the E_1 field (perpendicular to the laser beam) in the polar phase below 270 K, where the pyroelectric effect is huge. Because above 270 K there is no difference, the origin of the SHG signals may be connected to some diffuseness of the transition, to which SHG is more sensitive than the pyroelectric effect. On the other hand, above the transition point, no difference between SHG signals was detected for crystals with and without E_1 action. Moreover, the SHG signals should not appear above the low-temperature transition point, i.e., in the centrosymmetric antiferroelectric AFE2 phase. Although the investigated PH crystals were stoichiometric, we cannot exclude the existence of defects like vacancies in Pb and O substructures, dislocations, and other extended defects. Also, the SHG signals may originate from the domain walls or translational boundaries of the ferroelectric order [5,19]. Because the SHG technique employed operates in reflection mode, the influence of a skin layer should also be considered. Despite the mentioned caveats appearing when the SHG measurement method is used, it is also sensitive to reveal changes

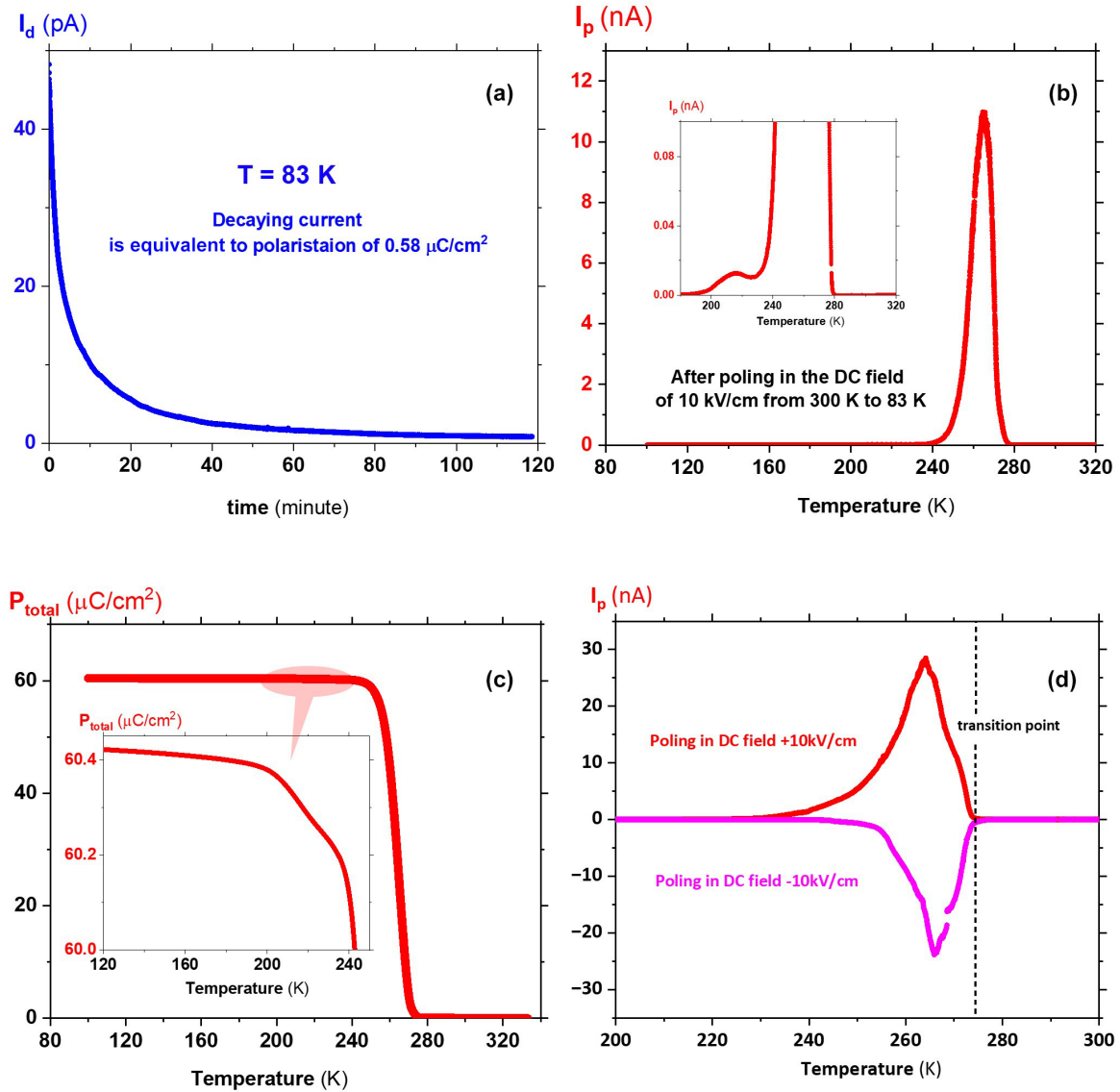


FIG. 2. (a) Time dependence of the depolarization current I_d at 83 K after crystal poling in the DC field. (b) Temperature changes of the current I_p on heating after depolarization at 83 K in 2 h. The I_p is the total pyroelectric current, which originates from the primary and secondary pyroelectric effect in the case of ferroelectric polarization [18]. The inset magnifies a part of the $I_p(T)$ that shows an additional anomaly at around 220 K. (c) Simultaneous temperature and time registration allowed the temperature evolution of the total polarization P_{total} to be determined. The inset in (b) represents an enlarged view of the polarization anomaly. (d) Reversibility of the pyroelectric signal for a crystal poled in a DC field of intensity +10 and -10 kV/cm. Nonsymmetrical runs may be due to the noncompletely reversible polarization owing, e.g., to its partial pinning by structural defects or not perfect ohmic contact electrode-crystal surface. A break (a jump of the signal) in the run for poling in the DC field of -10 kV/cm points to the first-order phase transition.

at transition points observed in several previously described experimental techniques.

It is well established that structural instabilities (soft phonon modes) are responsible for oxides perovskites' phase transitions. An example of the spectacular role of these instabilities is the existence of precursor polar clusters, known to appear already above T_c and be long-lived and quasistatic. Moreover, they are intrinsic and universal to ferroelectrics, antiferroelectrics, and antiferrodistortive systems [20]. The existence of these clusters is beyond the Landau-type description of structural phase transitions and results in strong nonlinearity and significant anharmonicity, leading to mode-mode (TA-TO) coupling. Due to such a competition between

interrelated instabilities, a local polarity appears. On the other hand, mixing the phonon bands corresponding to the polar (zone center) and tilting (zone boundary) instabilities is critical for the structure and antiferroelectric phase symmetry below T_c . In the article by Aramberri [21], it was shown that the ground state of PbZrO_3 combines antiphase tilts (R_4^+ mode), modulated polar distortions (Σ_2 band), and homogeneous polar distortions (Γ_4^- mode). In [21], it is also suggested that the same is true for PZ and PH. It consisted of the appearance, instead of the antipolar displacements of the Pb^{2+} ions top-top-down-down, of an uncompensated top-top-down arrangement corresponding to the polar (ferrielectric) state. Such uncompensated Pb^{2+} arrangement was proposed

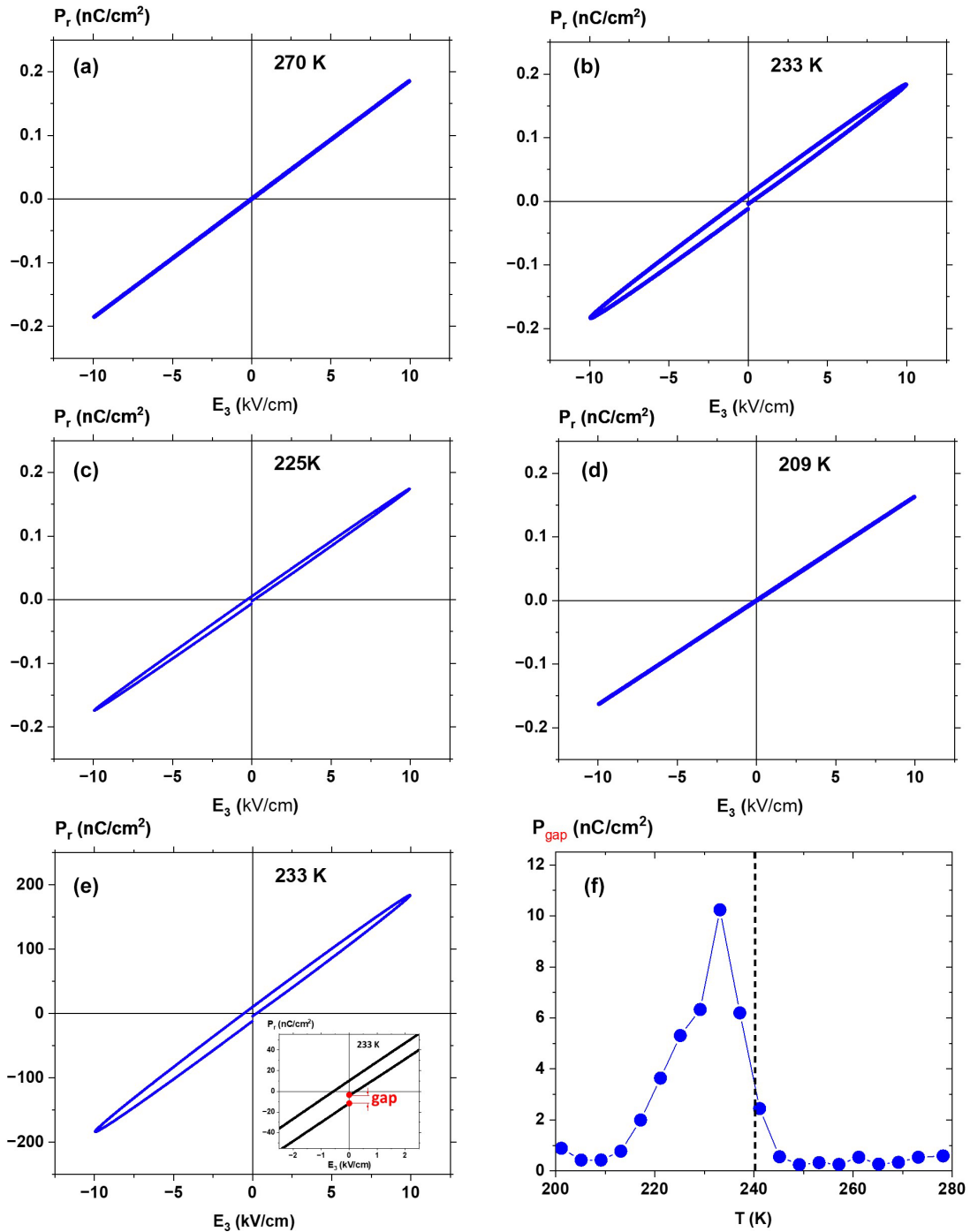


FIG. 3. (a)–(d) Temperature evolution, on cooling, of the polarization gap around the transition point near 240 K. At 233 K, below the transition, a distinct gap is visible, which appears due to the polar character of the transition. Far from the transition, the $P_r(E_3)$ run represents the linear function of an ideal dielectric. (e) An example of a $P_r(E_3)$ function with an inset showing the definition of the polarization gap. (f) The distinct change in the polarization gap P_{gap} values occurs below the transition near 240 K. The dashed line corresponds to the transition temperature where the pyroelectric current for pristine crystal starts increasing [see Fig. 1(b)].

to be a characteristic feature of the polar low-temperature mechanism for the low-temperature polarity phase, suggesting another phase transition. Interestingly, the oxygen ion's unconventional polarizability, which plays an essential role in perovskite ferroics, has not been considered in those mechanisms [22]. Understanding structural dynamics in lead-containing ABO_3 perovskites, like PbTiO_3 , PZ, and PH,

can also be based on purely mass-related effects. It was shown in [23] that the polar instability scales with the cell reduced mass, whereas the antiferroelectricity scales with the cell reduced mass, and the antiferroelectricity scales with the mass, mainly given by the polarizable transition metal B (Ti, Zr, Hf). When volume shrinks with an increasing mass of B ion, its polarizability decreases, and the polar instability dimin-

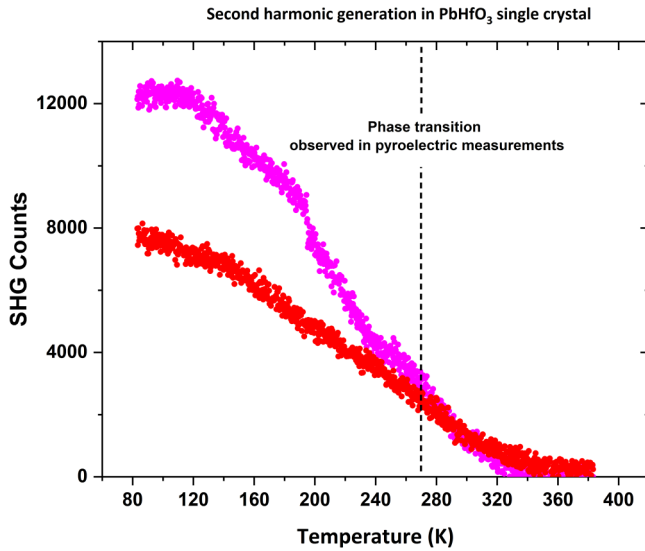


FIG. 4. Temperature dependence of the SHG signals for an unpoled (red points) and a poled sample in a DC electric field of 4 kV/cm perpendicular to the laser beam (magenta points) for the PH crystal, on heating. Dashed line marks the transition point as observed in the measurements of pyroelectric properties [see Figs. 2(b) and 2(d)]. The distinct difference in the runs is seen below the temperature point at which polar properties have been found, and gets the highest value of polarization [see Fig. 2(c)].

ishes. Hence, PZ appears to be related to structural dynamics between the PT and PH, reflecting the importance of the polarizable ion mass in determining ABO_3 dynamics. Here, it is worth presenting the effective ion radii of O^{2-} (140 Å), Hf^{4+} (71 Å), Zr^{4+} (72 Å), Pb^{2+} (119 Å) and atomic mass (in amu units) of O (16), Hf (178.5), Zr (91.2), and Pb (207.2). While the difference between the Hf^{4+} and Zr^{4+} ionic radii is negligible, Hf^{4+} is nearly twice as heavy as Zr^{4+} .

Although the observation of an additional phase transition in PH should not be surprising, as a similar one was observed in PZ [2]; the huge value of the polarization induced in the DC field is certainly unexpected. The small value of the low-temperature polarization in PZ, of the order of a few $nCcm^{-2}$, does not allow a clear assignment of the physical mechanism responsible for it. Indeed, it can be caused by symmetry changes throughout the crystal (throughout the originally antiferroelectric structure) but can also be related to polar interdomain boundaries (or other topological defects, such as vortices). It should be emphasized that, in the case of both PZ and PH crystals, the low-temperature polarity is an intrinsic polarity that appears without prepolarization. However, while the postulated value of the polarization resulting from *ab initio* considerations for PZ is several μCcm^{-2} and the experimentally observed one is only a few $nCcm^{-2}$, i.e., three orders of magnitude lower, in the case of the PH crystal, the theoretical and experimental values are of the same order.

At a glance, such a large difference in low-temperature polarity values between PZ and PH can be attributed primarily to the presence of the Hf^{4+} inside the oxygen octahedra. As discussed above, the huge difference in mass of the ions in the center of the oxygen octahedra may play an important role, as with the increase in mass, the polar instability diminishes

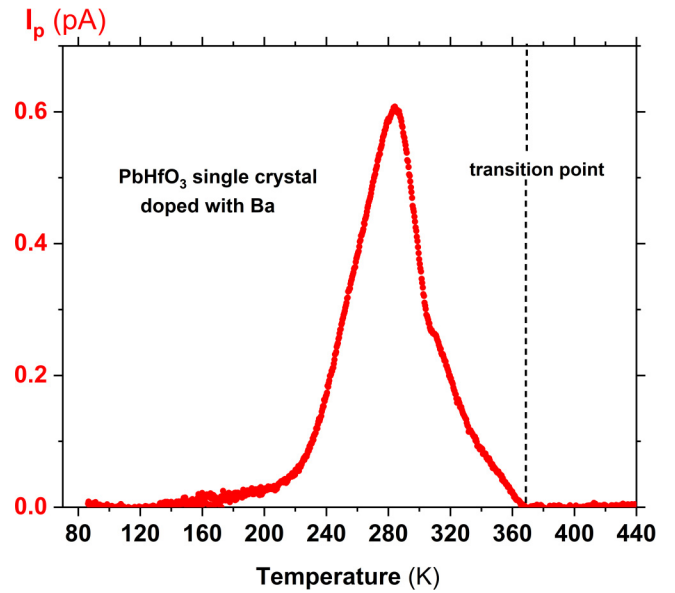


FIG. 5. The temperature dependence of the total pyroelectric current I_p on heating for the Ba-doped PH single crystal.

and leads, due to the high nonlinear polarizability of oxygen, to stable macroscopic polarization. Our preliminary research on doping the PH with the next heavy Ba^{2+} ions (137.3 amu) showed that the low-temperature transition occurs and shifts to a higher temperature, around 370 K, leaving the polarization at a low level of $37 nCcm^{-2}$. This value was determined from the pyroelectric effect shown in Fig. 5 for crystal poled in conditions similar to that used for PH.

Accordingly, if the mass does not play a role, the mechanisms explaining the huge polarization in pure PH can be related to the substructures of Pb^{2+} and O^{2-} ions. Pb^{2+} can easily be displaced from its structural positions as in $PbZr_{1-x}Ti_xO_3$ (PZT) compounds from the region of the morphotropic phase boundary (MPB) [24]. It was suggested that in the PZT with $x \sim 0.5$, the Pb^{2+} ions—easily displaced from their rhombohedral to monoclinic positions—are responsible for their huge piezoelectric (polar) properties. This was because of an unusual feature in the anisotropic displacement parameters (ADPs) (the anisotropic thermal parameters) for the Pb^{2+} ions, which form a flattened disk shape oriented to the [111] polar axis. Interestingly, such a disorder appeared to be characteristic of all PZT compositions. Because this disk shape was not temperature dependent, it was concluded that there is a static disorder in the Pb^{2+} substructure over three sites slightly off the [111] direction and towards the [100] direction. A key point was that the structure of a unit cell was not rhombohedral but monoclinic, with the Cm monoclinic space group symmetry. Although the mentioned disorder in Pb^{2+} was discussed in PZ, one cannot exclude it in PH.

Independent of the mechanism which leads to the huge polarity in PH, one can discuss a symmetry of this low-temperature phase. It can be done, e.g., based on the piezoelectric effect. We checked through the piezoelectric resonance method that the PH crystal poled in the [001] direction, exhibiting a huge resultant polarization at 83 K (i.e., polar axis), did not reveal piezoelectric properties. This means we

TABLE I. Overview of the piezoelectric matrix for the orthorhombic and monoclinic point and space group symmetries (*O*: orthorhombic; *M*: monoclinic).

Lattice system	Point group	Piezoelectric matrix ^a	Space groups
<i>O</i>	222	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$	<i>P</i> 222, <i>P</i> 222 ₁ , <i>P</i> 2 ₁ 2 ₁ 2, <i>P</i> 2 ₁ 2 ₁ 2 ₁ , <i>C</i> 222 ₁ , <i>C</i> 222, <i>F</i> 222, <i>I</i> 222, <i>I</i> 2 ₁ 2 ₁ 2 ₁
<i>O</i>	<i>mm</i> 2	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$	<i>Pmm</i> 2, <i>Pmc</i> 2 ₁ , <i>Pcc</i> 2, <i>Pma</i> 2, <i>Pca</i> 2 ₁ , <i>Pnc</i> 2, <i>Pmn</i> 2 ₁ , <i>Pba</i> 2, <i>Pna</i> 2 ₁ , <i>Pnn</i> 2, <i>Cmm</i> 2, <i>Cmc</i> 2 ₁ , <i>Ccc</i> 2, <i>Am</i> m2, <i>Ab</i> m2, <i>Ama</i> 2, <i>Aba</i> 2, <i>Fmm</i> 2, <i>Fdd</i> 2, <i>Im</i> m2, <i>Iba</i> 2, <i>Ima</i> 2
<i>M</i>	2	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix}$	<i>P</i> 2, <i>P</i> 2 ₁ , <i>C</i> 2
<i>M</i>	<i>m</i>	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{pmatrix}$	<i>Pm</i> , <i>Pc</i> , <i>Cm</i> , <i>Cc</i>

^aReference [18].

did not detect any piezoelectric signals corresponding to the d_{31} and d_{33} modules, which should have occurred for the sample used in experiments of a bar shape and with the $[001]_c$ pseudocubic edges. Assuming we can consider either ordering in the Pb^{2+} substructure (of monoclinic symmetry) or polar nanoregions (of monoclinic or orthorhombic symmetry), we can consider—based on the absence of the d_{31} and d_{33} piezoelectric coefficients—which of these symmetries can be realized (see Table I).

Analyzing Table I, it appears that there are only orthorhombic 222 and monoclinic 2 point groups symmetries, with a total of 12 space groups, in which the d_{31} and d_{33} are not active. Immediately, it means that the *Ima*2 space group (circled in red in Table I), postulated in [21] and belonging to the *mm*2 orthorhombic point group, cannot be realized in the low-temperature phase because both d_{33} and d_{31} are of nonzero values. Hence, a structural investigation of the PH crystal, also under a DC electric field action, has to be undertaken to find which of the orthorhombic phases describes the polar low-temperature phase in PH.

Finally, another mechanism for such large low-temperature polarity can be speculated upon. While we cannot exclude the presence of defects within the crystal volume, it is conceivable that rearrangements of oxygen vacancies under an electric field could lead to significant polarity and extremely high piezoelectricity, as reported in [25]. However, the performed tests of stoichiometry have not pointed to a distinct discrepancy from the ideal composition.

IV. CONCLUSIONS

In analogy to the case of lead zirconate, a low-temperature polar phase below 270 K has been discovered in antiferroelectric lead hafnium. In both cases, clear signs of a transition to this polar phase, with thermal hysteresis, were found from dielectric and pyroelectric measurements on pure crystals. In the case of PH, further evidence of such a transition was the measurement of the polarization gap around the transition point and the temperature evolution of the second harmonic generation signals. Interestingly, in contrast to PZ crystals, polarization in the DC field leads to a large polarization, manifesting in changes of $60 \mu\text{C cm}^{-2}$ at the transition point. Such large polarization was reversed by changing the sign of the polarizing DC field, pointing to ferroelectriclike properties.

ACKNOWLEDGMENTS

The authors thank Ł. Scheller from the University of Silesia in Katowice for technical assistance during experiments. This work was supported by the National Science Centre, Poland, Grant No. 2022/47/B/ST3/02778. J.K.Z. acknowledges support from *Academia Iuvenum*, Wrocław University of Science and Technology.

DATA AVAILABILITY

Data available from the authors upon reasonable request.

- [1] C. Kittel, Theory of antiferroelectric crystals, *Phys. Rev.* **82**, 729 (1951).
- [2] K. Roleder, G. Catalan, A. M. Glazer, J. S. Baker, J.-H. Ko, F. H. Naqvi, S. B. Junaid, A. Majchrowski, Z. Trybuła, J. Zareba *et al.*, Weak low-temperature polarity in a PbZrO_3 single crystal, *Phys. Rev. B* **107**, L140102 (2023).
- [3] W. N. Lawless, Glasslike thermal properties of antiferroelectric PbZrO_3 at low temperatures, *Phys. Rev. B* **30**, 6555 (1984).
- [4] G. Kugel, I. Jankowska-Sumara, S. Roleder, and J. Dec, High temperature raman light scattering in PbZrO_3 single crystals, *J. Kor. Phys. Soc.* **32**, S581 (1998).
- [5] Y. Liu, R. Niu, A. Majchrowski, K. Roleder, K. Cordero-Edwards, J. M. Cairney, J. Arbiol, and G. Catalan, Translational boundaries as incipient ferrielectric domains in antiferroelectric PbZrO_3 , *Phys. Rev. Lett.* **130**, 216801 (2023).
- [6] A. Bussmann-Holder, J.-H. Ko, A. Majchrowski, M. Górny, and K. Roleder, Precursor dynamics, incipient ferroelectricity and

- huge anharmonicity in antiferroelectric lead zirconate PbZrO_3 , *J. Phys.: Condens. Matter* **25**, 212202 (2013).
- [7] N. Zhang, M. Paściak, A. Glazer, J. Hlinka, M. Gutmann, H. A. Sparkes, T. Welberry, A. Majchrowski, K. Roleder, and Y. Xie, A neutron diffuse scattering study of PbZrO_3 and Zr-rich $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, *J. Appl. Crystallogr.* **48**, 1637 (2015).
- [8] J.-H. Ko, M. Górný, A. Majchrowski, K. Roleder, and A. Bussmann-Holder, Mode softening, precursor phenomena, and intermediate phases in PbZrO_3 , *Phys. Rev. B* **87**, 184110 (2013).
- [9] R. G. Burkovsky, A. K. Tagantsev, K. Vaideswaran, N. Setter, S. B. Vakhrushev, A. V. Filimonov, A. Shaganov, D. Andronikova, A. I. Rudskoy, A. Q. R. Baron *et al.*, Lattice dynamics and antiferroelectricity in PbZrO_3 tested by x-ray and Brillouin light scattering, *Phys. Rev. B* **90**, 144301 (2014).
- [10] A. K. Tagantsev, K. Vaideswaran, S. B. Vakhrushev, A. V. Filimonov, R. G. Burkovsky, A. Shaganov, D. Andronikova, A. I. Rudskoy, A. Q. R. Baron, H. Uchiyama, D. Chernyshov, A. Bosak, Z. Ujma, K. Roleder, A. Majchrowski, J.-H. Ko, and N. Setter, The origin of antiferroelectricity in PbZrO_3 , *Nat. Commun.* **4**, 2229 (2013).
- [11] J. Hlinka, T. Ostapchuk, E. Buixaderas, C. Kadlec, P. Kuzel, I. Gregora, J. Kroupa, M. Savinov, A. Klic, J. Drahokoupil *et al.*, Multiple soft-mode vibrations of lead zirconate, *Phys. Rev. Lett.* **112**, 197601 (2014).
- [12] D. Corker, A. Glazer, W. Kaminsky, R. Whatmore, J. Dec, and K. Roleder, Investigation into the crystal structure of the perovskite lead hafnate, PbHfO_3 , *Acta Crystallogr., Sect. B: Struct. Sci.* **54**, 18 (1998).
- [13] V. Madigout, J. Baudour, F. Bouree, C. Favotto, M. Roubin, and G. Nihoul, Crystallographic structure of lead hafnate (PbHfO_3) from neutron powder diffraction and electron microscopy, *Philos. Mag. A* **79**, 847 (1999).
- [14] S. Huband, A. M. Glazer, K. Roleder, A. Majchrowski, and P. A. Thomas, Crystallographic and optical study of PbHfO_3 crystals, *J. Appl. Crystallogr.* **50**, 378 (2017).
- [15] R. G. Burkovsky, I. Bronwald, D. Andronikova, G. Lityagin, J. Piecha, S.-M. Souliou, A. Majchrowski, A. Filimonov, A. Rudskoy, K. Roleder *et al.*, Triggered incommensurate transition in PbHfO_3 , *Phys. Rev. B* **100**, 014107 (2019).
- [16] M. Knyazeva, D. Andronikova, G. Lityagin, I. Bronwald, P. Paraskevas, A. Majchrowski, K. Roleder, A. Filimonov, and R. Burkovsky, Phase transitions in lead hafnate under high pressure, *Phys. Solid State* **61**, 1759 (2019).
- [17] A. Bosak, V. Svitlyk, A. Arakcheeva, R. Burkovsky, V. Diadkin, K. Roleder, and D. Chernyshov, Incommensurate crystal structure of PbHfO_3 , *Acta Crystallogr., Sect. B: Struct. Sci.* **76**, 7 (2020).
- [18] J. F. Nye, *Physical Properties of Crystals: Their Representation by Tensors and Matrices* (Oxford University Press, New York, 1985).
- [19] X.-K. Wei, A. K. Tagantsev, A. Kvasov, K. Roleder, C.-L. Jia, and N. Setter, Ferroelectric translational antiphase boundaries in nonpolar materials, *Nat. Commun.* **5**, 3031 (2014).
- [20] A. Bussmann-Holder, T. H. Kim, B. W. Lee, J.-H. Ko, A. Majchrowski, A. Soszyński, and K. Roleder, Phase transitions and interrelated instabilities in PbHfO_3 single crystals, *J. Phys.: Condens. Matter* **27**, 105901 (2015).
- [21] H. Aramberri, C. Cazorla, M. Stengel, and J. Íñiguez, On the possibility that PbZrO_3 not be antiferroelectric, *npj Comput. Mater.* **7**, 196 (2021).
- [22] A. Bussmann-Holder, The polarizability model for ferroelectricity in perovskite oxides, *J. Phys.: Condens. Matter* **24**, 273202 (2012).
- [23] A. Bussmann-Holder, K. Roleder, and J.-H. Ko, Instabilities in the ferro- and antiferroelectric lead perovskites driven by transition metal ion mass: From PbTiO_3 via PbZrO_3 to PbHfO_3 , *J. Phys.: Condens. Matter* **26**, 275402 (2014).
- [24] A. M. Glazer, P. A. Thomas, K. Z. Baba-Kishi, G. K. H. Pang, and C. W. Tai, Influence of short-range and long-range order on the evolution of the morphotropic phase boundary in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, *Phys. Rev. B* **70**, 184123 (2004).
- [25] D.-S. Park, M. Hadad, L. Riemer, R. Ignatans, D. Spirito, V. Esposito, V. Tileli, N. Gauquelin, D. Chezganov, and D. Jannis, Induced giant piezoelectricity in centrosymmetric oxides, *Science* **375**, 653 (2022).