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Ferroelectricity in perovskite $HoMnO_3$ and $YMnO_3$

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Ferroelectricity is observed in orthorhombic $HoMnO_3$ and $YMnO_3$ at the magnetic lock-in transitions into an *E*-type structure or an incommensurate phase with a temperature independent wave vector, respectively. In $HoMnO_3$, the ferroelectric polarization strongly depends on the external magnetic field, indicating the involvement of the rare earth moment order in this compound. The results are discussed within the framework of recent theoretical models, in particular, the double exchange driven polar displacements predicted for *E*-type magnetic structures.

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I. INTRODUCTION

Multiferroic magnetoelectric manganites have attracted increasing attention because of the coexistence of ferroelectric and magnetic orders, the control of polarization by external and internal magnetic fields as well as by external pressure, the role of spin frustration in stabilizing improper ferroelectricity, and the rich phase diagrams with cascades of magnetic and ferroelectric phase transitions upon changing temperature or magnetic fields.[1,2] In hexagonal manganites, $RMnO_3$ (R=Y, Ho to Lu), ferroelectricity arises well above the antiferromagnetic (AFM) ordering temperature and the coupling between the ferroelectric (FE) order and the frustrated AFM Mn spin structure is indirect (the linear magnetoelectric effect is forbidden by symmetry) and mediated by magnetoelastic interactions.[3–5] In contrast, the ferroelectricity in orthorhombic $TbMnO_3$ and the kagomé staircase compound $Ni_3V_2O_8$ has been shown to be triggered by a magnetic phase transition from a sinusoidal to a helical spin-density wave with the spatial inversion symmetry broken in the latter phase.[6,7] The magnetoelastic coupling leads to a distortion of the lattice with a net FE polarization perpendicular to the propagation vector of the spin-density wave and the axis of rotation of the helical modulation.[8] This empirical picture is based on symmetry considerations; it suggests a trilinear coupling of the magnetic order parameters and the FE polarization, and it is supported by a recent microscopic model for $Ni_3V_2O_8$.[9] The orthorhombic RMn_2O_5 rare earth manganites also show ferroelectricity at the magnetic lock-in transition into a commensurate magnetic structure. The microscopic origin of the FE order has yet to be understood; however, it was suggested that the magnetic frustration among the Mn spins is reduced by a displacement of oxygen and manganese ions with a macroscopic polarization along the orthorhombic b axis.[10,11] In a more detailed investigation of the spin structure of $TbMn_2O_5$ and YMn_2O_5, Chapon *et al.* have explained the ferroelectricity in the commensurate phase of RMn_2O_5 as induced by an acentric spin-density wave.[12,13]

The magnitude of the FE polarization in the above mentioned manganites and vanadates is relatively small with typical values of 100 nC/cm^2 at low temperatures. This was attributed in part to the small antisymmetric Dzyaloshinskii-Moriya spin-spin interaction resulting from the spin-orbit coupling that plays a major role in the ferroelectrics with helical magnetic structures.[14] Alternative physical mechanisms resulting in FE order induced by magnetic modulations with possibly larger values of the FE polarization have therefore been searched for. Sergienko *et al.*[15] have recently proposed the existence of FE order in the *E*-type magnetic structure of orthorhombic $HoMnO_3$ and other compounds and predicted an order of magnitude larger polarization as compared to the manganites discussed in the previous paragraph. The microscopic mechanism is a competition between elastic energy and the energy gain due to the (virtual) hopping of Mn e_g electrons along the ferromagnetically aligned moments of a Mn zigzag chain in the *E*-type magnetic structure. Strong dielectric anomalies and an increase of the dielectric constant of up to 60% at the magnetic transitions of orthorhombic $HoMnO_3$ and $YMnO_3$ have indeed been reported by us[16] suggesting the possible existence of FE. We have therefore decided to search for FE in orthorhombic $HoMnO_3$ and $YMnO_3$ and assess the role of the rare earth element. We prove the existence of a macroscopic FE polarization P in orthorhombic $HoMnO_3$ and $YMnO_3$ by measuring the pyroelectric current that arises from a change of $P(T)$ during cooling or heating through the magnetic and FE phase transitions.

The $RMnO_3$ manganites can be synthesized in the orthorhombic structure for all rare earth ions; however, for R =Ho to Lu and Y the perovskite structure is metastable and the synthesis has to be conducted under high-pressure conditions.[16,17] The magnetic structures of $HoMnO_3$ and $YMnO_3$ have been investigated by neutron scattering. Both compounds undergo a phase transition into an incommensurate (IC) magnetic structure at $T_N \approx 42$ K and at lower temperature the magnetic order locks into a commensurate *E*-type order ($HoMnO_3$) (Ref. 18) or into an incommensurate phase with a temperature independent modulation vector ($YMnO_3$).[19] The stability of the *E*-type magnetic order in $HoMnO_3$ as the ground state configuration was recently confirmed by first principles calculations.[20] Dielectric anomalies are observed at all magnetic phase transitions.[16]

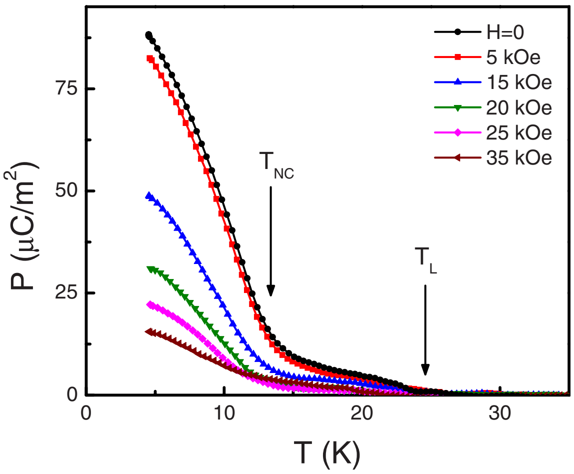

FIG. 1. (Color online) Temperature dependence of the ferroelectric polarization P of HoMnO$_3$ in different magnetic fields H (increasing from top to bottom curve).

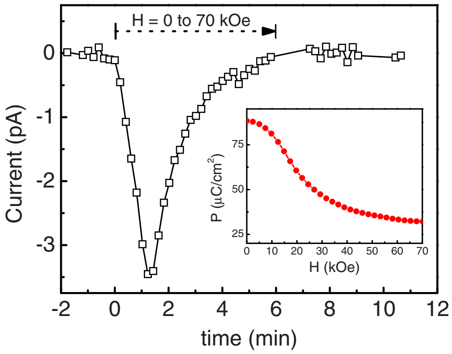

FIG. 2. (Color online) Decrease of FE polarization of HoMnO$_3$ with increasing magnetic field at 4.5 K. the main panel shows the discharging current. Inset: Ferroelectric polarization $P(H)$.

II. EXPERIMENT

The samples of HoMnO$_3$ and YMnO$_3$ used in this paper have been synthesized under high-pressure conditions as described elsewhere.[16] X-ray spectra indicate a pure orthorhombic phase with no detectable reflections of impurity phases. Polycrystalline pellets of high density have been shaped for pyroelectric current measurements. The typical sample thickness was 0.4 mm and the contact area was of the order of 8 mm^2. The physical property measurement system (Quantum Design) was used for temperature and magnetic field control. The pyroelectric current was measured upon heating in zero electric field employing the Keithley 6517A electrometer after cooling the sample in electric fields of up to 5 kV/cm and shortening the contacts at the lowest temperature for 15 min. The polarization was calculated by integrating the pyroelectric current. Although the samples are polycrystalline (single crystals of high-pressure synthesized samples are not available), the current signal was clearly detected. The measurement represents an average of the polarization over all possible grain orientations and the data provide a lower limit for the actual FE polarization that is supposed to be aligned with the a axis (space group $Pbnm$).[15]

III. RESULTS AND DISCUSSION

The temperature dependence of the FE polarization of HoMnO$_3$ calculated from the pyroelectric current data is shown in Fig. 1 at different magnetic fields. The spontaneous polarization $\vec{P}$ starts to grow at T_L=26 K, the temperature of the lock-in transition into the AFM E phase. The neutron scattering data[18] show that the magnetic moments of the Mn ions change continuously below T_N in passing through T_L and the Ho moment increases smoothly below T_L. The magnitude of $\vec{P}$ is small, in contrast to the large value predicted by Sergienko *et al.*,[15] and it increases rapidly only below 15 K, the temperature at which a major change in the magnetic structure of the Ho moments has been reported.[18] According to the neutron scattering results, the collinear AFM order of the Ho moments oriented along the b axis sets in at T_L with the sublattice magnetization increasing significantly at lower T. At T_{NC}=15 K, the Ho moments rotate in the a-b plane and form a noncollinear magnetic structure.[18] The polarization (Fig. 1) exhibits a significant increase at this temperature, suggesting an involvement of the rare earth magnetic order in stabilizing the FE displacements. The temperature dependence of P is indeed qualitatively similar to that of the Ho moment.[18] The FE polarization is dramatically reduced in external magnetic fields as shown in Figs. 1 and 2 up to 70 kOe. Increasing the magnetic field at a rate of 200 Oe/s at 4.5 K, after poling the FE domains during cooling, indeed generates a current that proves the decrease of the FE polarization as shown in Fig. 2. The inset of Fig. 2 displays the estimated polarization. In agreement with the magnetic field dependence of the dielectric constant,[16] $P(H)$ experiences the major decrease above 10 kOe where a metamagnetic transition (alignment of the Ho moments with the field) had been reported.[16,18]

The strong correlation of the polarization change below 15 K with the Ho magnetic order and its sensitivity to external magnetic fields raises the question about the microscopic origin of the ferroelectricity and the role of Mn spins and rare earth magnetic moments. According to the recent theoretical proposal,[15] the rare earth moment should not be essential for the FE order in the compound, but magnetoelastic effects along the ferromagnetic zigzag chains of Mn spins are responsible for the FE distortions. We have, therefore, investigated rare-earth free orthorhombic YMnO$_3$ with respect to ferroelectricity. The pyroelectric current measured on a polycrystalline sample indeed reveals a FE transition taking place at 28 K. The measured polarization is shown in Fig. 3. Unlike the HoMnO$_3$, the polarization of YMnO$_3$ does not depend on the magnetic field up to 70 kOe. The FE polarization in YMnO$_3$ is larger than that determined for HoMnO$_3$ and it arises exactly at the lock-in temperature T_L =28 K of the incommensurate Mn spin-density wave. Neutron scattering experiments suggested that below T_L, the spin modulation is still incommensurate with q=0.434 along the b axis but it is locked into a temperature independent value.[19] The origin of ferroelectricity in orthorhombic YMnO$_3$, however, is difficult to understand within this collinear IC mag-

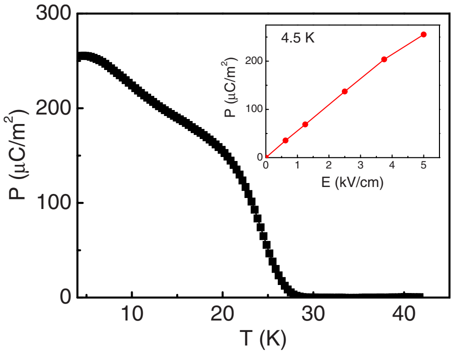

FIG. 3. (Color online) Temperature dependence of the ferroelectric polarization P of orthorhombic $YMnO_3$. The inset shows the maximum polarization at 4.5 K for different poling fields.

netic order scheme. This issue will be discussed in detail below.

The value of the measured polarization is largely affected by the polycrystalline nature of the high-pressure synthesized samples. However, large single crystals of high-pressure synthesized orthorhombic $RMnO_3$ are not available and all experiments have to be conducted using dense ceramic samples. While this is not a principal problem and ferroelectric ceramics are well known and even commercially available, a few cautious measures have to be applied to avoid experimental artifacts affecting the results and interpretations. The electrical current i between the two electrodes attached to a parallel plate dielectric can be expressed as

$$i = C\frac{dV}{dt} + A\frac{dP}{dt} + \frac{V}{R}, \tag{1}$$

where V is the (time dependent) applied voltage, $C = \varepsilon\varepsilon_0 A/L$ is the capacitance, A and L are the contact area and sample thickness, respectively, and R is the sample resistance. The three terms in Eq. (1) are the capacitive, ferroelectric, and resistive currents. The samples of $HoMnO_3$ and $YMnO_3$ investigated in this work are highly resistive with a dc resistance at low temperatures larger than $10^9\ \Omega$. This excludes any significant resistive currents and it indicates the high quality of the compounds. In order to separate the current that is due to a sole change of the ferroelectric polarization, all measurements have been conducted at zero bias voltage with increasing temperature (thus excluding the capacitive current) after cooling the samples in a constant electric field. Before starting the pyroelectric current measurements at the lowest temperature, the electrodes have been shortened for up to 15 min in order to release any charges in the system. This procedure excludes any artifact due to the change of large electric fields, trapped charges, etc., as discussed earlier in the case of extremely inhomogeneous systems (for example, ferroelectric copolymers).[21] The possibility that ferroelectricity arises in the grain boundaries or the surface of the grains cannot be completely ignored. However, it appears very unlikely that the pyroelectric current measured between the two metallic electrodes is solely generated by polarization charges in the grain boundary. The total area of the grain boundaries underneath the electrode is small as compared to the contact area and any contribution from a possible polarization in the grain boundaries is expected to be negligible.

Due to the random orientation of the grains in the polycrystalline sample, the measured polarization has to be lower than the intrinsic P for a single grain or FE domain. First, the measurement can only provide data for the component of $\vec{P}$ perpendicular to the contact surface averaging over all possible grain orientations since it is clear that the FE polarization is directed along one of the principal crystallographic orientations. According to the theory of Sergienko *et al.*,[15] $\vec{P}$ is aligned with the orthorhombic a axis. Secondly, cooling in strong electric field is necessary to align the FE domains within a single grain. The electric field component in the direction of the FE polarization, however, depends on the grain orientation and it decreases if the angle between the electric field and $\vec{P}$ increases. Therefore, grains with a less perfect FE domain alignment will always exist, causing the macroscopic polarization to be smaller than that for a properly oriented single crystal. In addition, even with a perfect grain orientation the minimum electric field E_{min} to align all domains along the field direction is not known and the maximum applied field of 5 kV/cm in this experiment may be smaller than E_{min}. Indeed, plotting the maximum P of $YMnO_3$ at the lowest temperature as a function of the poling electric field (inset of Fig. 3) reveals that the saturation polarization was not achieved in the current experiment. Increasing the poling field further is experimentally difficult due to the limited strength of the sample and the environment with respect to a dielectric breakdown. Single crystals of orthorhombic $HoMnO_3$ and $YMnO_3$ are highly desirable but not yet available. Alternatively, the growth of thin epitaxial films on appropriate substrates with the orientation of $\vec{P}$ perpendicular to the film surface will avoid the random grain problem and could be used to determine the intrinsic values of the FE polarization.

The microscopic origin of the FE order in orthorhombic $RMnO_3$ is still a matter of discussion. Several models have been proposed to explain the ferroelectricity induced by magnetic orders. The phase transition from sinusoidal spin modulation to a helical magnetic structure was shown by symmetry arguments and Landau theory to break the spatial inversion symmetry and allow for a macroscopic FE polarization through a third order coupling between the magnetic order parameter and the FE polarization.[6–8] For the orthorhombic YMn_2O_5, Chapon *et al.*[13] have shown that a noncentrosymmetric magnetic structure arises at the magnetic lock-in transition within a system of AFM aligned zigzag chains of Mn^{4+} and Mn^{3+} spins propagating along the a axis with an appropriate spin orientation and a phase factor. The FE polarization then arises from a strong magnetoelastic coupling. Evidence of sizable magnetoelastic effects has been found recently in large anomalies of the thermal expansivities at the FE transitions in RMn_2O_5.[11] The most recent proposal involves the double exchange mechanism virtually coupling the e_g electrons of neighboring Mn^{3+} ions with the same direction of the magnetic moment that competes with the elastic energy.[15] In an E-type magnetic modulation with ferromagnetic zigzag chains of Mn spins, this mechanism can stabilize ferroelectricity through a cooperative displacement of oxygen ions generating a macroscopic polarization along the orthorhombic *a* axis. This model could explain the observed ferroelectricity in $HoMnO_3$.

Our data for $HoMnO_3$ shown in Fig. 1, however, indicate that the case is more complex because of the involvement of the rare earth magnetic moment. The Ho moment apparently plays a crucial role and is responsible for the rapid increase of the FE polarization below 15 K (Fig. 1). While, in principle, the FE displacement below T_L can be explained by the double exchange mechanism,[15] the details of the temperature dependence of P and its strong magnetic field dependence need further discussion. The rare earth moments in $HoMnO_3$ experience a spin reorientation at $T_{NC}=15$ K,[18] changing their collinear alignment with the *b* axis to a noncollinear magnetic structure below T_{NC}. This noncollinear structure can give rise to an additional FE displacement in a sense discussed by Mostovoy[8] and Harris and co-workers[6,7] through magnetoelastic interactions. The noncollinear Ho moment order below T_{NC} would allow a FE displacement along the *a* axis (perpendicular to the propagation vector of the *E*-type modulation and the rotation axis between the two spin arrangements), which is incidentally the same direction as follows from the double exchange mechanism involving the Mn spin order. Therefore, we conclude that, in addition to the Mn spin order, the rare earth magnetic order plays a major role in stabilizing ferroelectricity in $HoMnO_3$ at low temperatures. This is further supported by the strong magnetic field dependence of the polarization in $HoMnO_3$ above 10 kOe similar to the one observed for the dielectric constant data.[16] The metamagnetic transition aligning the Ho moments with the field decreases the angle between the Ho moments. Since the polarization arising from the noncollinear Ho moment order is proportional to the vector product of the two moments,[8] the FE polarization will decrease with the decreasing angle between them.

The ferroelectricity observed in orthorhombic $YMnO_3$ (Fig. 3) is more difficult to explain based on the published data for the magnetic structure of the Mn spins. Neutron scattering experiments have been interpreted with contradicting results. Quezel *et al.*[22] proposed a helical Mn spin order with an antiparallel spin arrangement in the *a*-*c* plane and an incommensurate modulation along the *b* axis with a relatively small propagation vector ($q_y=0.079$). Although this spin structure involves a helical modulation, it cannot give rise to a FE displacement within the Landau theory proposed by Mostovoy[8] and others since the propagation vector and the rotation axis of the helical modulation are parallel and the corresponding cross product of both vectors results to zero. Later, Munoz *et al.*[19] revised the magnetic structure of $YMnO_3$ and proposed an incommensurate sinusoidal spin order propagating along the orthorhombic *b* axis with the wave vector of $q_y=0.434$. This magnetic structure is characterized by zigzag chains of parallel spins in the *a*-*b* plane directed along the *a* axis. The major difference with respect to the *E*-type commensurate order is the modulation of the magnitude of the spins in neighboring zigzag chains that follows the incommensurate wave. In fact, the *E*-type spin structure follows for the commensurate value $q_y=0.5$. The double exchange mechanism proposed by Sergienko *et al.*[15] does apply to a single FM zigzag chain and may result in a local distortion along the chain direction with a corresponding polarization. However, due to the incommensurate modulation of the Mn moments along the *b* axis, the folding direction of the FM zigzag chains is reversed every few unit cells, resulting in a reversal of the local polarization in the chain.[23] The magnetic structure and the resulting in-chain polarization are sketched in Fig. 4(b) and compared with the *E*-type structure of Fig. 4(a). The character of the dielectric order in the case of $YMnO_3$ should be antiferroelectric with a periodic modulation of the polarization according to the IC magnetic modulation. The two polarizations shown at the right and left unit cells in Fig. 4(b) are opposite in sign since the folding directions of the two FM zigzag chains correspond to the two magnetic domains of the commensurate *E*-type magnetic order.[23] Within the double exchange model, the FE polarization does change sign if the magnetic domain is reversed.[15]

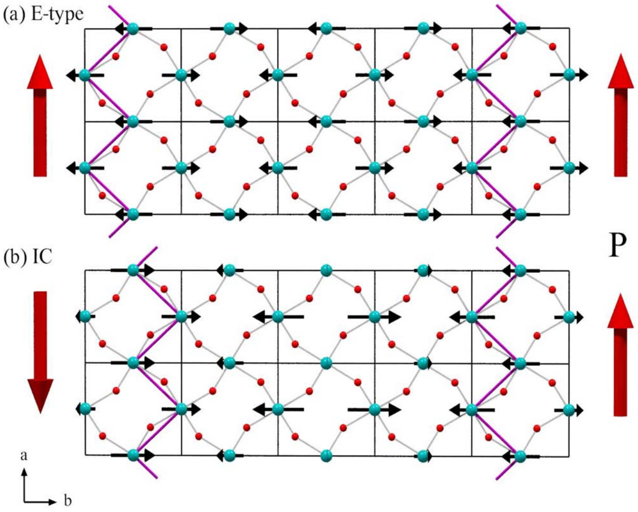

FIG. 4. (Color online) Magnetic order and ferroelectric polarization arising from the double exchange mechanism for (a) the *E*-type commensurate structure ($HoMnO_3$) and (b) the sinusoidal incommensurate order proposed for $YMnO_3$. (Ref. 19). Large spheres: Mn ions with spins. Small spheres: oxygen ions. The FM aligned zigzag chains are shown for the first and last unit cells and the local polarization in these chains is indicated by the large vertical arrows.

While the macroscopic FE polarization was clearly observed in our experiments below the lock-in transition of orthorhombic $YMnO_3$, the physical mechanism leading to ferroelectricity is not clear. It appears conceivable to assume that, similar to $TbMnO_3$ or $HoMnO_3$, the ferroelectricity in $YMnO_3$ is improper and the primary order parameter is of magnetic origin driving the FE distortion through a polar magnetic order and the spin-lattice coupling. Since the magnetic structures derived from both neutron scattering investigations[19,22] do not support a macroscopic polarization based on the mechanisms proposed by Mostovoy[8] and Sergienko *et al.*,[15] an alternative theoretical description (for example, by extending the existing models or by developing new theories) or a reconsideration of the magnetic structure seems to be necessary. In the phase diagram of orthorhombic

$R\mathrm{MnO_3}$,[24] the $\mathrm{YMnO_3}$ is close to $\mathrm{HoMnO_3}$ on one side and $\mathrm{DyMnO_3}$ and $\mathrm{TbMnO_3}$ on the other side. For $\mathrm{TbMnO_3}$, the ferroelectricity was explained by the IC helical magnetic structure of the Mn spins as verified by neutron scattering data.[6] High quality single crystals are needed to resolve the magnetic structure in great detail and to distinguish the noncollinear helical modulation from a collinear sinusoidal spin arrangement. Unfortunately, single crystals of metastable $R\mathrm{MnO_3}$ compounds synthesized under high-pressure conditions are not available and neutron scattering experiments on polycrystalline samples or powders may not reveal the exact orientation of the spins. Therefore, it is possible that the magnetic order in $\mathrm{YMnO_3}$ is similar to that of $\mathrm{TbMnO_3}$, locking into a helical structure below $T_L=28$ K that would explain the ferroelectricity below this temperature. Alternatively, since the size of the $\mathrm{Y^{3+}}$ ion is almost identical to the size of $\mathrm{Ho^{3+}}$ and the Mn-O-Mn bond angle is very similar for both compounds, the *E*-type magnetic structure could be realized also in $\mathrm{YMnO_3}$ in which case the ferroelectricity can be explained by the double exchange mechanism discussed by Sergienko *et al.*[15] However, this assumption is only valid if the magnetic modulation below T_L is commensurate (*E* type), in contrast to the most recent neutron scattering results.[19] Further and more detailed investigations of the magnetic structure of $\mathrm{YMnO_3}$ are necessary to resolve the conflicts and to find an explanation for the observed ferroelectricity in the compound.

IV. SUMMARY

We have proven the existence of ferroelectric order below the magnetic lock-in transition in orthorhombic $\mathrm{HoMnO_3}$ and $\mathrm{YMnO_3}$. The FE polarization detected in both compounds is relatively small. *P* values of other orthorhombic $R\mathrm{MnO_3}$ and $R\mathrm{Mn_2O_5}$ are distinctively larger. The value of 250 $\mu\mathrm{C/m^2}$ of $\mathrm{YMnO_3}$ is more comparable to the FE polarization of $\mathrm{Ni_3V_2O_8}$. Thus, the expectation of a 2 orders of magnitude higher polarization in the *E*-type structure[15] cannot be verified in the case of $\mathrm{HoMnO_3}$ and/or $\mathrm{YMnO_3}$. It is unlikely that the polycrystalline nature of our samples and the factors discussed above can account for such a dramatic reduction of the polarization. While large single crystals of the compounds are not available, it is suggested to investigate the FE properties of thin films grown on appropriate substrates.

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