1. Introduction

Ferroelectric materials have been intensely studied because of fundamental physics involving underlying mechanisms behind non-polar to polar structural phase transitions as well as various technological applications such as non-volatile memory devices and piezoelectric sensors. Recently, the development of novel ferroelectrics has been accelerated since Benedek and Fennie rationalized novel design principles of ferroelectric layered perovskite oxides utilizing rotations of oxygen-coordinated octahedra. In their work, they theoretically revisited the origin of polar distortions in \( n = 2 \) Ruddlesden–Popper (RP) layered perovskites \( \text{Ca}_n\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_n\text{Mn}_2\text{O}_7 \), where \( n \) is the number of perovskite layers per block. They proposed that in these layered perovskites, a spontaneous polarization is induced symmetrically and energetically by a combination of two non-polar rotation modes of octahedra via trilinear coupling. This is called hybrid improper ferroelectricity. Such crystal chemistry-based guidelines for lifting inversion symmetry up to a bunch of novel acenetic, polar and ferroelectric RP oxides. For example, ferroelectric switching was experimentally demonstrated for \( n = 2 \) RP phases \( \text{Ca}_n\text{Sr}(\text{Ti},\text{Mn})_2\text{O}_7 \) and \( \text{Sr}_2\text{Zr}_2\text{O}_7 \), and \( \text{Sr}(\text{Ba},\text{Ca})_2\text{Sn}_2\text{O}_7 \). In addition, \( \text{Ca}(\text{Sr},\text{Ti})_2(\text{Ti},\text{Fe})_2\text{O}_7 \) was reported to be polar and potentially ferroelectric. It was also reported that acentricity is induced by oxygen octahedral rotations in \( A \)-site ordered \( n = 1 \) RP titanates \( \text{ARTiO}_4 \) (\( A = \text{H}, \text{Li}, \text{Na}, \text{K}; R = \text{rare earth} \)).

Hybrid improper ferroelectricity is also possible for \( n = 2 \) Dion–Jacobson (DJ) phases, which is another type of layered perovskites consisting of primitive stacking of adjacent perovskite blocks, in contrast to body-centered stacking in RP phases. In spite of the difference in stacking fashions, ferroelectricity induced by oxygen octahedral rotations was also theoretically predicted for \( n = 2 \) DJ phases \( \text{ARB}_2\text{O}_7 \) (\( A = \text{Rb}, \text{Cs}, R = \text{La}, \text{Nd}, B = \text{Nb}, \text{Ta} \)), and indeed, these oxides were proven to be polar by means of synchrotron X-ray diffraction (XRD), neutron diffraction, and optical second harmonic generation measurements. However, ferroelectric switching has not been demonstrated yet for these \( n = 2 \) DJ phases. On the other hand, ferroelectricity has been reported for Bi-containing DJ phases such as \( \text{RbBiNb}_2\text{O}_7 \) and \( \text{CsBiNb}_2\text{O}_7 \), in which \( 6s^2 \) stereochemically active lone-pair electrons in Bi can play a crucial role in the ferroelectricity. It was also reported that ferroelectricity is induced by interfacial coupling effects in tailor-made nanosheets composed of \( n = 2 \) DJ phases.

Here, we focus on Bi-free \( n = 2 \) DJ phases \( \text{CsNdNb}_2\text{O}_7 \) and \( \text{RbNdNb}_2\text{O}_7 \). Their ferroelectricity is induced almost purely by octahedral rotations as predicted theoretically. Detailed structural analyses for these compounds were recently performed by Zhu et al. The crystal structure of \( \text{CsNdNb}_2\text{O}_7 \) belongs to a polar space group \( P \bar{2} \text{am} \) with the \( a \) and \( c \) axes pointing to the directions along the spontaneous polarization and perpendicular to the layer, respectively, and a combination of synchrotron X-ray and neutron diffraction recently clarified temperature-induced phase transitions from \( P \bar{2} \text{am} \) to \( C2'/m \) at 625 K to \( P4/mmm \) at 800 K. On the other hand, \( \text{RbNdNb}_2\text{O}_7 \) crystallizes into a structure with polar \( I2\text{cm} \) space group symmetry, and shows phase transitions from \( I2\text{cm} \) to \( C\text{mca} \) at 790 K to \( I4/mcm \) at 865 K. The structural analyses suggested that these compounds are polar and potentially ferroelectric at room temperature, but their ferroelectricity is not reported yet.

In this work, we prepared highly dense and insulating pellets of the \( n = 2 \) DJ niobates \( \text{CsNdNb}_2\text{O}_7 \) and \( \text{RbNdNb}_2\text{O}_7 \) by a conventional solid-state reaction method, and demonstrated their ferroelectric switching. The polycrystalline pellets were characterized by synchrotron XRD. Electric polarization–field (\( P–E \)) curve measurements were performed at room temperature to demonstrate their ferroelectricity. The ceramic pellets of \( \text{CsNdNb}_2\text{O}_7 \) and \( \text{RbNdNb}_2\text{O}_7 \) show the clear \( P–E \) hysteresis loops with the remanent polarizations much larger than those observed for polycrystalline samples of other hybrid improper ferroelectrics such as \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Sr}_2\text{Zr}_2\text{O}_7 \). Impedance...
spectroscopy revealed that the ceramics pellets are highly insulating in contrast to the ceramic pellets of \( n = 2 \) DJ niobates reported in previous studies, allowing for the clear observation of ferroelectric switching of CsNdNb\(_2\)O\(_7\) and RbNdNb\(_2\)O\(_7\). The polar to non-polar phase transition at 625 K in CsNdNb\(_2\)O\(_7\) was detected by the measurement of temperature-dependent dielectric constants, while no phase transition was observed for RbNdNb\(_2\)O\(_7\) throughout the measured temperature range (\( \approx \)773 K). These results are in good agreement with the recent structural analyses.\(^{22} \)

2. Experimental procedures

The powder and polycrystalline pellet samples of CsNdNb\(_2\)O\(_7\) and RbNdNb\(_2\)O\(_7\) were prepared via a conventional solid-state reaction method. Reagent-grade Cs\(_2\)CO\(_3\) (99.9%; Kojundo Chemical Laboratory Co. Ltd.), Rb\(_2\)CO\(_3\) (99%; Kojundo Chemical Laboratory Co. Ltd.), Nd\(_2\)O\(_3\) (99.9%; Nippon Yttrium Co. Ltd.), and Nb\(_2\)O\(_5\) (99.9%; Kojundo Chemical Laboratory Co. Ltd.) powders were used as starting materials. The Nd\(_2\)O\(_3\) and Nb\(_2\)O\(_5\) powders were heated at 900 °C for 12 h to eliminate water and carbon dioxide adsorbed on the powders prior to weighing. A 50 mol% excess amount of Cs\(_2\)CO\(_3\) and Rb\(_2\)CO\(_3\) were added to a mixture of the starting materials to compensate for the loss due to the alkaline evaporation during heating. The mixtures were ground for several tens of minutes with an agate mortar using ethanol as dispersion solvent, followed by drying at 353 K for 3 h. The mixture pellets were obtained by uniaxial pressing at 40 MPa for 1 min and subsequent cold isotropic pressing at 200 MPa for 5 min. The pellets were put on a Pt plate in an alumina crucible with a lid, and calcined at 1123 K for 12 h. The calcined pellets were ground, thoroughly mixed, pelletized again, and then sintered at 1273 K for 48 h. The phase purity of the samples was confirmed using a laboratory XRD equipment (D8 ADVANCE; Bruker AXS GmbH). Relative density of the pellets was determined by the Archimedes' method.

High-resolution synchrotron XRD patterns were taken at room temperature with a Debye–Scherer camera with MYTHEN solid-state detectors installed at the BL02B2 beamline of Spring-8.\(^{27} \) The ground powder samples were housed in Lindeman capillary tubes with an inner diameter of 0.1 mm. The capillary tubes were rotated continuously during the measurements to diminish the effect of preferred orientation. We used an X-ray beam monochromated at \( \lambda = 0.670 479 \text{ Å} \) or 0.669 111 Å. The wavelength is selected so as to prevent the effect of Nb K-edge absorption (0.6532 Å) and detect the diffraction originating from the largest lattice spacing (\( \approx 11 \text{ Å} \)) within the 2θ angle range for the beamline (\( \geq 2 \)). Rietveld refinements\(^{26} \) were performed for the XRD pattern of CsNdNb\(_2\)O\(_7\) with a \( P2_1/am \) model\(^{26} \) excluding the region of the impurity peaks. The resultant fit provides small reliability factors: \( R_w = 6.79\% \), \( R_B = 2.02\% \), and \( \chi^2 = 10.44 \). On the other hand, as for RbNdNb\(_2\)O\(_7\), all the peaks except for the subtle NdNbO\(_4\) impurity signals (2.3 wt%) were well-fitted using an \( I2cm \) model\(^{21} \) with small reliability factors: \( R_w = 11.5\% \), \( R_B = 3.41\% \), and \( \chi^2 = 5.93 \).

3. Results and discussion

Figures 1(a) and 1(b) show the room-temperature synchrotron XRD patterns for the CsNdNb\(_2\)O\(_7\) and RbNdNb\(_2\)O\(_7\) powders, respectively, as well as fitting curves obtained by Rietveld refinements. The diffraction peaks for CsNdNb\(_2\)O\(_7\) are indexed by assuming \( P2_1/am \) symmetry, although a trace amount of NdNbO\(_4\) impurity (0.3 wt%) was present. The Rietveld refinements were performed for the XRD pattern of CsNdNb\(_2\)O\(_7\) with a \( P2_1/am \) model\(^{26} \) excluding the region of the impurity peaks. The resultant fit provides small reliability factors: \( R_w = 6.79\% \), \( R_B = 2.02\% \), and \( \chi^2 = 10.44 \). On the other hand, as for RbNdNb\(_2\)O\(_7\), all the peaks except for the subtle NdNbO\(_4\) impurity signals (2.3 wt%) were well-fitted using an \( I2cm \) model\(^{21} \) with small reliability factors: \( R_w = 11.5\% \), \( R_B = 3.41\% \), and \( \chi^2 = 5.93 \).

The refined structural parameters shown in Tables I and II are in good agreement with the recent structural analyses.\(^{22} \)

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**Fig. 1.** (Color online) Synchrotron X-ray diffraction patterns (red open circles) at room temperature for (a) CsNdNb\(_2\)O\(_7\) and (b) RbNdNb\(_2\)O\(_7\), and fitting curves (black lines) obtained by Rietveld refinements using \( P2_1/am \) and \( I2cm \) models for CsNdNb\(_2\)O\(_7\) and RbNdNb\(_2\)O\(_7\), respectively. The green ticks and blue lines represent the positions of Bragg diffractions and the difference between the observed and simulated intensity, respectively. The insets illustrate the schematics of refined structures. The solid lines indicate unit cells. The refined structural parameters are summarized in Tables I and II for CsNdNb\(_2\)O\(_7\) and RbNdNb\(_2\)O\(_7\), respectively.
Table I. Structural parameters of CsNdNb₂O₇ at room temperature obtained from Rietveld refinement with a P₄mm space group model against the synchrotron XRD data shown in Fig. 1(a).

| Atom  | Site | x    | y    | z    | Uᵣ or Uₑq (Å²) |
|-------|------|------|------|------|----------------|
| Cs⁺   | 2b   | 0.75²⁰ | 0.7369(3) | 1/2 | 0.0183(4) |
| Nd⁴⁺  | 2a   | 0.7591(5) | 0.7473(3) | 0   | 0.0072(15) |
| Nb⁴⁺  | 4c   | 0.2422(6) | 0.7505(3) | 0.2017(4) | 0.0073(14) |
| O²⁻   | 8c   | 0.238(2) | 0.8008(9) | 0.6420(3) | 0.0055(12) |
| O²⁻   | 8c   | 0.4325(13) | 0.4436(12) | 0.1867(4) | 0.0120(12) |
| O²⁻   | 8c   | 0.007(3) | 0.018(2)  | 0.1425(4) | =Uₑq(021) |
| O²⁻   | 2a   | 0.2153(19) | 0.6815(11) | 0   | =Uₑq(011) |

Space group; P mmm (No. 26), Z = 2. The occupancy parameter is fixed to unity for all atoms. a) Refined anisotropically. b) Fixed to define an origin of the polar a-axis. Cell parameters: a = 5.470 4986(6) Å, b = 5.449 7887(6) Å, and c = 11.159 235(14) Å. Rwp = 6.79%, Rfi = 2.02%, and χ² = 10.44.

Table II. Structural parameters of RbNdNb₂O₇ at room temperature obtained from Rietveld refinement with a P2₁2₁2₁ space group model against synchrotron XRD data shown in Fig. 1(b).

| Atom  | Site | x    | y    | z    | Uᵣ or Uₑq (Å²) |
|-------|------|------|------|------|----------------|
| Rb⁷⁺  | 4a   | 0.75²⁰ | 0    | 0    | 0.0277(18) |
| Nd⁴⁺  | 4b   | 0.2379(18) | 0.4995(11) | 1/2 | 0.0089(3) |
| Nb⁴⁺  | 8c   | 0.7608(18) | 0.5010(13) | 0.6466(4) | 0.0100(4) |
| O²⁻   | 8c   | 0.757(4) | 0.546(2)  | 0.4327(2) | 0.0042(15) |
| O²⁻   | 8c   | 0.581(3) | 0.799(3)  | 0.6556(4) | =Uₑq(011) |
| O²⁻   | 8c   | 0.957(3) | 0.235(4)  | 0.6754(4) | =Uₑq(011) |
| O²⁻   | 4b   | 0.266(6) | 0.065(3)  | 1/2 | =Uₑq(011) |

Space group; P mmm (No. 46), Z = 4. The occupancy parameter is fixed to unity for all atoms. a) Refined anisotropically. b) Fixed to define an origin of the polar a-axis. Cell parameters: a = 5.442 25(2) Å, b = 5.429 77(2) Å, and c = 21.963 23(7) Å. Rwp = 11.5%, Rfi = 3.41%, and χ² = 5.93.

agreement with those reported in the previous X-ray and neutron diffraction studies. Bond valence sums of the cations calculated for the refined structures are 1.1 for Cs, 2.9 for Nd, and 4.9 for Nb in CsNdNb₂O₇ and 0.9 for Rb, 3.1 for Nd, and 5.0 for Nb in RbNdNb₂O₇, all of which are very close to the formal valences. The origin of their spontaneous polarizations and the structural difference between the P₂₁2₁2₁ and Pmcm phases are briefly reviewed in the appendix section in line with the previous theoretical and experimental studies.

The inset of Fig. 2(a) shows the cross-sectional SEM image of the CsNdNb₂O₇ pellet, confirming the high densification degree. The microstructure with parallel stripes is similar to that observed by piezo-response force microscopy for the CsBiNb₂O₇ pellet prepared by a spark plasma sintering method. The insets of Figs. 2(b) and 2(c) show the appearance of the pellet samples of CsNdNb₂O₇ and RbNdNb₂O₇, respectively. Both pellets are translucent because of their small thickness (200–300 μm) and high relative density (98%–99%). The light violet color of the pellets stems from optical absorption corresponding to Nd 4f–4f transitions.

Figure 2(a) displays the P–E curves for the CsNdNb₂O₇ pellet at room temperature. The P–E curves clearly exhibit hysteresis behavior characteristic of ferroelectric materials, free from piscis-shaped loops due to leakage current, which are often observed for n = 2 DJ compounds. Only a few recent reports have indisputably demonstrated ferroelectricity for polar n = 2 DJ phases. This is partially ascribed to the fact that this class of samples often show electric leakage and breakdown, hampering the observation of obvious P–E hysteresis loops to evidence ferroelectricity. In a sharp contrast, the present pellets are highly insulating, as referred to the impedance results hereafter. The switching component of polarization (Pₑq) measured by a PUND method is plotted against E for CsNdNb₂O₇ and RbNdNb₂O₇ in Figs. 2(b) and 2(c), respectively. The observed hysteresis curves verify the ferroelectricity of CsNdNb₂O₇ and RbNdNb₂O₇. The remanent polarization (Pᵣ), which is a value of Pₑq at zero field, is increased with an increase in the electric field amplitude, and Pᵣ is not saturated yet even for the maximum field amplitude for both the samples. The higher fields were not applicable due to electric breakdown. The maximum Pᵣ values were recorded as 2.5 and 2.1 μC cm⁻² for CsNdNb₂O₇ and RbNdNb₂O₇, respectively, which are much smaller than the theoretically calculated polarization, Pₑq, of 29 and 30 μC cm⁻² for CsNdNb₂O₇ and RbNdNb₂O₇, respectively. This is because the samples are polycrystalline and the polarizations are not saturated yet due to their high coercive electric fields. Compared to the present compounds, higher remanent polarizations were reported for Bi-containing n = 2 DJ phases CsBiNb₂O₇ and RbBiNb₂O₇ (~10 μC cm⁻²), partly because they have large theoretical polarizations owing to the 6s² lone-pair electrons in Bi⁵⁺ (Pₑq = 36–48 μC cm⁻² for CsBiNb₂O₇ and RbBiNb₂O₇), and/or because a non-switching component of polarizations originating from electric leakage might be included in the reported remanent polarizations.

It should be noted that the remanent polarizations of CsNdNb₂O₇ and RbNdNb₂O₇ are several times larger than those observed for the polycrystalline samples of other hybrid improper ferroelectrics such as RP layered perovskites Ca₃Ti₂O₇, Sr₃Zr₂O₇, and Sr₃Sn₂O₇, as summarized in Table III. Now we discuss the reasons behind this, although it is hard to strictly compare their remanent polarization characteristics because the polarization was recorded with different electric field amplitude (180–320 kV cm⁻¹). One might think that the larger remanent polarizations of the two DJ phases simply reflect the fact that Pₑq, i.e. the theoretically predicted potential polarization, is higher for the DJ phases than for the RP phases (see Table III). However, the ratios Pₑq/Pₑq are also larger for the DJ phases than the RP phases, which excludes the magnitude of potential polarizations from one of the main reasons. Another reason may be that the coercive electric fields, Eₑq, are significantly lower for the DJ phases than for the RP phases, as shown in Table III. In general, coercive fields depend on various factors such as the Curie temperatures (see Table III), the energy barriers against polarization switching and domain wall motions, and the orientation of polarization axes of each grain in polycrystalline pellets. To get an insight into the larger polarizations observed for the DJ phases, further experimental studies with single crystals and theoretical investigations on switching pathways and domain wall motions are required.

Impedance spectroscopy was performed to investigate the electrical properties and dielectric constants. Figure 3(a) presents a Nyquist plot for the CsNdNb₂O₇ pellet at room...
The observed semicircle was analyzed using an equivalent circuit model comprising a single, parallel RC element, resulting in a fairly good fit with a resistance of $\sim 13 \, \Omega$. The insulating nature of the pellet sample is confirmed by the high resistance. Such a highly insulating property allows for the clear observation of the polarization switching shown in Fig. 2. The electrical conductivity of the pellet is $9.4 \times 10^{-9} \, \text{S cm}^{-1}$, which is much lower than that reported for $n = 2$ DJ phase CsBiNb$_2$O$_7$ ($\sim 10^{-3} \, \text{S cm}^{-1}$) due to significant proton conductivity. The real and imaginary parts of relative dielectric constants, $\varepsilon'_r$ and $\varepsilon''_r$, respectively, were estimated with the equivalent circuit model. Figure 3(b) plots $\varepsilon'_r$ at room temperature as a function of frequency. There is little frequency dependence of $\varepsilon'_r$; $\varepsilon''_r$, while a weak upturn is observed below $10^3 \, \text{Hz}$. Figure 3(c) shows the temperature dependence of $\varepsilon'_r$ and the dielectric loss, tan $\delta = \varepsilon''_r/\varepsilon'_r$, for the CsNdNb$_2$O$_7$ pellet measured at $f = 10^6 \, \text{Hz}$. A dielectric anomaly is observed at 625 K both on heating and cooling with a small thermal hysteresis. This observation of anomaly coincides with the recent structural analysis revealing that CsNdNb$_2$O$_7$ exhibits a phase transition from polar $P2_1$ am to non-polar $Cm$ phases at 625 K on heating. The dielectric loss is low at room temperature (tan $\delta \approx 0.1$). The overall increase in tan $\delta$ with increasing temperature indicates that the
electrical leakage becomes significant at higher temperatures. On the other hand, $\epsilon_0$ of the RbNdNb$_2$O$_7$ pellet is almost constant ($\epsilon_0 = 36-40$) without any dielectric anomaly throughout the temperature range studied here ($\leq 773$ K), in accordance with the recent report that RbNdNb$_2$O$_7$ keeps polar $I2cm$ symmetry up to 790 K. The RbNdNb$_2$O$_7$ pellet also shows a low dielectric loss at room temperature ($\tan \delta \approx 0.1$), revealing its highly insulating nature. The value of $\epsilon_0$ at room temperature in our samples are comparable to those in other $n = 2$ DJ niobates ($\epsilon_0 = 10-60$).

4. Conclusion

Through the observation of polarization switching by electric field, we clearly demonstrate the ferroelectricity of $n = 2$ DJ layered perovskites CsNdNb$_2$O$_7$ and RbNdNb$_2$O$_7$, which have been regarded as potentially ferroelectric phases according to the previous structural analyses so far. The remnant polarizations of the polycrystalline pellets (2–3 $\mu$C cm$^{-2}$) are much larger than those of other hybrid improper ferroelectrics with layered perovskite structures. The clear P–E hysteresis loops were obtained thanks to the high electrical resistivity, as confirmed by the impedance spectroscopy. The temperature-dependent relative dielectric constants exhibit the anomaly at 625 K for CsNdNb$_2$O$_7$ reflecting a ferroelectric phase transition, while no dielectric anomaly was detected for RbNdNb$_2$O$_7$ up to the highest temperature studied here (773 K).

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Appendix: The origin of spontaneous polarizations and the structural difference between the $P2_1/am$ and $I2cm$ phases

Here let us review the origin of spontaneous polarizations in the $P2_1/am$ and $I2cm$ phases and their structural difference. The $P2_1/am$ symmetry is established by a direct sum of reducible representations (irreps) $M_3$ and $M_5^+$ for the aristotype, undistorted $P4/mmm$ phase. The atomic displacement transforming like $M_3$ corresponds to oxygen octahedral tilting represented by $a' a' c^0$ in Glazer notation, and the $M_5^+$ distortion corresponds to rotation represented by $a' a' a c^+$; therefore, the $P2_1/am$ phase shows an $a' a' c^-$-type of octahedral rotation. The rotation and tilting distortions with a wavenumber vector at the M point $(\frac{1}{2}, \frac{1}{2}, 0)$ lead to a cell expansion to a $\sqrt{2}a_1 \times \sqrt{2}a_1 \times c_1$ metric, where $a_1$ and $c_1$ are lattice constants of the aristotype $P4/mmm$ phase. The $P2_1/am$ structure also encompasses a polar distortion transforming like an irrep $\Gamma_5^+$, which generates $P$ along the $a$ axis. The polar $\Gamma_5^+$ distortion is induced by a combination of the $M_3^-$ and $M_5^-$ distortions in terms of both symmetry and energy lowering; a product of order parameters of the $M_3^-$, $M_5^-$, and $\Gamma_5^+$ distortions is invariant under the symmetry operations of $P4/mmm$, so the Landau energy expansion includes a trilinear coupling term:

$$ F_{ui} \propto \eta(M_3^-)\eta(M_5^+)P, $$

where $\eta(M_3^-)$ and $\eta(M_5^+)$ are order parameters of the $M_3^-$ and $M_5^+$ distortions, respectively, and the polarization $P$ is proportional to the order parameter of the $\Gamma_5^+$ distortion.

In the $I2cm$ structure, each perovskite slab shows an $a' a' c^0$-type of octahedral rotation, but the sense of rotation and tilting is opposite to that in the adjacent slabs. Therefore, the rotation pattern is represented as $a' a' c^-/(a' a' c^0)$ using an extended version of Glazer notation defined in Ref. 21, where rotation patterns of the lower and higher slabs are written before and behind a slash, and the opposite sense of rotation and tilting is denoted by a prefactor minus sign. The $I2cm$ symmetry is established by a direct sum of irreps $A_5^-$ and $A_5^+$ for the $P4/mmm$ phase. The atomic displacement transforming like the irrep $A_5^-$ corresponds to an $a' a' a'^{-}-a' c'^{-}$-type of tilting, and the $A_5^+$ distortion corresponds to an $a' a' a'^{+}-a' c'^{+}$-type of rotation. The distortion modes at the A point ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) result in a cell expansion to a $\sqrt{2}a_1 \times \sqrt{2}a_1 \times 2c_1$ metric. Hence, the conventional unit cell of the $I2cm$ phase is twice as long as that of the $P2_1/am$ phase [see the insets of Figs. 1(a) and 1(b)]. A polar $\Gamma_5^+$ distortion is induced by the following trilinear coupling involving the $A_5^-$ and $A_5^+$ modes, the form of which is similar to that for the $P2_1/am$ phase:

$$ F_{ui} \propto \eta(A_5^-)\eta(A_5^+)P, $$

where $\eta(A_5^-)$ and $\eta(A_5^+)$ are order parameters of the $A_5^-$ and $A_5^+$ distortions, respectively.

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