

Competing Structural Instabilities in the Ruddlesden–Popper Derivatives HRTiO₄ (R = Rare Earths): Oxygen Octahedral Rotations Inducing Noncentrosymmetricity and Layer Sliding Retaining Centrosymmetricity

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Supporting Information

ABSTRACT: We report the observation of noncentrosymmetricity in the family of $HRTiO_4$ (R = Eu, Gd, Dy) layered oxides possessing a Ruddlesden–Popper derivative structure, by second harmonic generation and synchrotron X-ray diffraction with the support of density functional theory calculations. These oxides were previously thought to possess inversion symmetry. Here, inversion symmetry is lifted by rotations of the oxygen-coordinated octahedra, a mechanism that is not active in simple perovskites. We observe a competition between rotations of the oxygen octahedra and sliding of a combined unit of perovskite–rocksalt–perovskite blocks at the proton layers. For the smaller rare earth ions, R = Eu, Gd, and Dy, which favor the octahedral rotations,



noncentrosymmetricity is present but the sliding is absent. For the larger rare earth ions, R = Nd and Sm, the octahedral rotations are absent, but the sliding at the proton layers is present to optimize the length and direction of hydrogen bonding in the crystal structure. The study reveals a new mechanism for inducing noncentrosymmetricity in layered oxides, and chemical–structural effects related to rare earth ion size and hydrogen bonding that can turn this mechanism on and off. We construct a phase diagram of temperature versus rare earth ionic radius for the HRTiO₄ family.

1. INTRODUCTION

Simple perovskite oxides, ABO_3 , exhibit a plethora of phenomena such as pyroelectricity, ferroelectricity, piezoelectricity, and nonlinear optical effects that rely on broken inversion symmetry in the crystal structure. These effects enable many important technologies such as ultrasonic imaging, precision actuation, and micromotors for biomedical applications, nonvolatile memory, electro-optic switches that power the Internet, new laser wavelengths, and infrared cameras. Nonetheless, of all the synthesized perovskites and layered oxides that we have surveyed in the International Crystal Structure Database,¹ a small fraction of ~0.4% is noncentrosymmetric. The vast majority of these noncentrosymmetric perovskite oxides rely on the mechanism of second-order Jahn–Teller (JT) distortion^{2–4} of the BO₆ octahedron and/or a polarizable lone pair cation at the A-cation site.⁵ While the majority of the complex oxides also exhibit oxygen octahedral rotations (OOR),⁶ these distortions do not break inversion symmetry in simple ABO₃ perovskites.⁷ However, OOR can exclusively⁸ or in combination with first-order JT distortion⁹ break inversion symmetry in layered oxides, and thus, they have the potential to expand the family of noncentrosymmetric layered oxides.

Article

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Rondinelli and Fennie¹⁰ and Benedek and Fennie¹¹ have recently proposed that various combinations of OOR are capable of lifting inversion symmetry in layered oxides and perovskite superlattices, making them noncentrosymmetric. Many of these predictions have recently been experimentally verified. For example, in the case of A-site ordered n = 1 Ruddlesden–Popper (RP) NaRTiO₄¹² and its derivative LiRTiO₄ (R = rare earths), ¹³ it has been shown that an $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ (Glazer notation)⁶ type of OOR in combination with A-site cation ordering makes these compounds noncentrosymmetric.¹⁴ Straver et al.¹⁵ have also demonstrated noncentrosymmetricity in n = 2 Dion-Jacobson (DJ) compounds, $ALaB_2O_7$ (A = Cs, Rb; B = Ta, Nb) by means of an $a^{-}b^{0}c^{+}$ -type of OOR. Li et al.¹⁶ and Chen et al.¹⁷ have established ferroelectricity in DJ compounds RbBiNb2O7 and CsBiNb₂O₇, respectively. Oh et al.¹⁸ have reported a pathway of different OOR involved in the ferroelectric and ferroelastic switching of (Ca, Sr)₃Ti₂O₇. Senn et al.¹⁹ have demonstrated hybrid improper ferroelectricity by OOR in Ca₃Mn₂O₇ and Ca₃Ti₂O₇. Pitcher et al.²⁰ have reported a chemical route to engineer octahedral tilts in multiferroic $(Ca_{\nu}Sr_{1-\nu})_{115}Tb_{185}Fe_2O_7$ by alloying with $Ca_3Ti_2O_7$. Kim et al.^{21'} have likewise confirmed noncentrosymmetricity in layered honeycomb-structured PbMnTeO₆. Overall, layered perovskites are being extensively studied for noncentrosymmetricity.

In the present work, we focus on another family of layered oxides, HRTiO₄, which are A-site ordered n = 1 RP derivative compounds. HRTiO₄ is a family of RP derivative compounds in which the HO layers between the TiO₆ perovskite layers are expected to be very different structurally and chemically from the LiO and NaO layers in LiRTiO₄¹³ and NaRTiO₄¹² which we have proven to be noncentrosymmetric so far, because of the covalent character of the hydroxyl bonds stronger than the chemical bonds between alkaline and oxides ions. The LiRTiO4 and NaRTiO₄ crystal structures differ, in that the LiO layer is antifluorite-type while the NaO layer is rocksalt-type.^{12,13} In spite of this structural difference, we observed that the type of OOR is the same, i.e., $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$, in the two families with the magnitude of OOR depending on the size of the rare earth ions. So far, HRTiO₄ compounds have been studied for applications in photocatalysis and as intercalation compounds, but they have all been considered to be centrosymmetric and, hence, neither polar nor piezoelectric. Nishimoto et al. have reported a P4/nmm crystal structure for HRTiO₄ (R = La, Nd)²² and $P2_1/c$ for HYTiO₄^{23,24} at ambient temperature. Also, Byeon et al.²⁵ have reported a I4/nmm crystal structure for HSmTiO₄. Silyukov et al.²⁶ have recently studied HRTiO₄ (R = La, Nd) in the temperature range of 25 to 1000 °C and have reported structural phase transitions involving dehydration in these compounds. Low-temperature (below room temperature) structural phase transitions and related properties have not been reported thus far.

Figure 1 summarizes the structures and space groups of the HRTiO₄ family reported in this work. Beginning from the high temperature centrosymmetric phase in the space group P4/nmm (Figure 1a) with no OOR, which has been reported previously,^{24,25} different phase transitions are observed for different rare earths, as the size of the rare earth ion decreases from highest to lowest radius in the order Nd, Sm, Eu, Gd, and Dy. The compounds with R = Eu, Gd, and Dy transform to the noncentrosymmetric space group $P\overline{42}_1m$ (Figure 1b) due to the $a^-b^0c^0/b^0a^-c^0$ -type of OORs, which also have been reported for LiRTiO₄ and NaRTiO₄. The compounds with R = Nd and Sm transform into another centrosymmetric space group, *Cmcm*, at



Figure 1. Schematic drawings comparing the noncentrosymmetric and centrosymmetric crystal structures of HRTiO₄. (a) The *P*4/*nmm* crystal structure of HRTiO₄ (for R = Nd and Sm at room temperature and for R = Eu, Gd, and Dy at high temperatures). (b) The $P\overline{4}2_1m$ structure with the $a^-b^0c^0/b^0a^-c^0$ -type octahedral rotation pattern for R = Eu, Gd, and Dy at room temperature. (c) The *Cmcm* structure for R = Nd and Sm below room temperature. The regions around the proton layers are highlighted for (d) *P*4/*nmm*, (e) *P* $\overline{4}2_1m$, and (f) *Cmcm* structures. The hydrogen atoms occupy partially at the least symmetric site (16k for the *P*4/*nmm* structure and 8*f* for the *P* $\overline{4}2_1m$ and *Cmcm* structures) to retain stoichiometry at a distance of about 1 Å from the oxide ions in the OH layers.

lower temperatures with no OOR; but, sliding of a combined unit of the perovskite—rocksalt—perovskite blocks by half the lattice parameter a in the [100] crystallographic direction is observed at the proton layer, as shown in Figure 1c.

In this work, on the basis of the experimental results combined with first-principles density functional theory (DFT) calculations, we conclude that the coordination environment of rare earth ions induces OORs in these compounds: the smaller rare earth ions are underbonded to oxide ions, facilitating OORs, while the larger rare earth ions are overbonded and do not require the OORs. In addition, when OORs do not occur, the layer sliding occurs at the proton layers so that hydrogen bonding is optimized in terms of its length and direction in the crystal structure, as demonstrated by our DFT calculations. The regions around the proton layers are magnified for P4/nmm, $P\overline{42}_1m$, and *Cmcm* structures in Figure 1d–f, where hydrogen atoms are located at the positions conjectured on the basis of the results of DFT calculations.

We report the results of first-principles phonon calculations for HRTiO₄ (R = La and Y) to search their stable structures in Section 3.1. In Sections 3.2 and 3.3 to follow, we present the evidence of noncentrosymmetricity and new crystal structures of the HRTiO₄ family for the three small rare earth ions, Eu, Gd, and Dy, in decreasing order of ionic radius. In Section 3.4, we discuss the two largest rare earth ions studied, Nd and Sm, and confirm the presence of inversion symmetry and the phenomenon of layer sliding. We conclude the study in Section 4.

2. EXPERIMENTAL SECTION

2.1. First-Principles Calculations. First-principles calculations were performed using the projector augmented-wave (PAW) method^{27,28} and the PBEsol functional^{29–31} as implemented in the VASP code.^{32–34} PAW data sets with radial cutoffs 0.4, 1.5, 1.8, 1.2, and



Figure 2. (a-e) Schematics of representative crystal structures of groups obtained in the stable structure search for HLaTiO₄ and HYTiO₄ can be classified [see the main text]. The dashed lines between O and H atoms indicate hydrogen bonds. The dotted rectangle in (a) indicates a unit cell with an in-plane lattice parameter a_p . Focusing on the dotted rectangles in (b) and (c), we can clearly see that the structures of Group 3 are made via sliding of the perovskite—rocksalt—perovskite blocks in the structures of Group 2 by half of a_p at the proton layers. Total energies of the structures obtained in the stable structure search for (f) HLaTiO₄ and (g) HYTiO₄.

0.8 Å for H, La, Y, Ti, and O, respectively, were used with a cutoff energy of 550 eV for plane waves. The following states were treated as valence electrons: 1s for H; 5s, 5p, 5d, and 6s for La; 4s, 4p, 4d, and 5s for Y; 3s, 3p, 3d, and 4s for Ti; 2s and 2p for O. The lattice parameters and internal coordinates were optimized until the residual stress and forces converged down to 0.01 GPa and 1 meV/ Å, respectively.

The phonon frequency was calculated by PHONOPY code from the calculated force constants.³⁵ More stable structures were searched for HRTiO₄ with R = La and Y by finding unstable phonon modes, according to a method described by Togo and Tanaka.³⁶ First, phonon frequencies were calculated at the Brillouin zone center and boundaries for the parent RP *P*4/*nmm* structures, in which HO exhibits a rocksalt-type configuration as shown in Figure 2a, and unstable phonon modes were found. Next, the parent structure was distorted according to the eigenvectors of the unstable phonon modes so as to obtain "child" structures with lower total energy and symmetry. Then, phonon calculations were performed for the child structures after the structural optimization. In those cases, for which the unstable phonon modes were found for them, this procedure was repeated. Otherwise, the structure was found to be dynamically stable. The "family-tree" diagram was completed when we cannot see any more unstable phonon modes.

We also examined zero-point vibration contribution to the total energies of the dynamical stable structures since the compounds studied here contain light hydrogen atoms. However, we found that the consideration of the zero-point energy effects did not change our calculation results qualitatively and, hence, our conclusions. Therefore, we will present the calculation results that were obtained without taking into account the zero-point energy contribution.

In addition, the total energies for some of the HRTiO₄ structures were obtained in the family tree calculations for HLaTiO₄ and HYTiO₄ using the PBE-D3 functional,^{37,38} which contains van der Waals correction. The calculation results indicate that, upon use of PBE-D3 instead of the PBEsol functional, on the basis of which the analysis has been done, the energy difference between the structures with and without layer sliding becomes smaller; that is, the energy gains by the slides become smaller. However, the structures with the slides are still the most stable for $HLaTiO_4$, and the structures with OORs and slides are the most stable for $HYTiO_4$. Thus, the main conclusions of the DFT calculations do not change.

2.2. Materials Synthesis. Polycrystalline HRTiO₄ (R = Nd, Sm, Eu, Gd, and Dy) were synthesized by ion exchange from NaRTiO₄ following the technique developed by Schaak and Mallouk.³⁹ First, NaRTiO₄ was synthesized by solid state reaction from chemical grade polycrystalline precursors, Na₂CO₃, R₂O₃, and TiO₂. The methodology has been described by Sen Gupta et al.¹³ Following this, HRTiO₄ (R = Nd, Sm, Eu, Gd, and Dy) was synthesized by ion exchange of NaRTiO₄ with 0.1 M HNO₃ for about 48 h.

2.3. Characterization. Temperature-dependent high resolution SXRD patterns were obtained in the Bragg–Brentano optical system at the 11-BMB beamline of the Advanced Photon Source at Argonne National Laboratory. The diffractometer has a multianalyzer detection assemblage. It consists of 12 Si (111) crystal analyzers and LaCl₃ scintillation detectors.⁴⁰ The wavelength of the incident X-rays was 0.4143 and 0.459 Å. Rietveld refinement of the SXRD patterns was done using the RIETAN-FP code.⁴¹

For the optical second harmonic generation (SHG) probe technique,⁴² a Ti-sapphire laser with an output of 800 nm, 80 fs pulses at 2 kHz repetition rate was used. Optical SHG is a nonlinear probing technique in which two photons with fields E_j and E_k of frequency ω and polarization directions j and k, respectively, interact with a noncentrosymmetric material (through a nonlinear tensor d_{ijk}) to create a nonlinear polarization $P_i^{2\omega}$ of frequency 2ω in the *i* direction. The SHG intensity, $I^{2\omega}$, is detected in the experiment. The equation governing the relationship between the detected SHG intensity, $I^{2\omega}$, and this nonlinear process is

$$I^{2\omega} \propto (P_i^{2\omega})^2 \propto (d_{ijk} E_i^{\omega} E_k^{\omega})^2 \tag{1}$$

Since the nonlinear tensor, d_{ijk} is zero when inversion symmetry is present, SHG probing is an effective method to differentiate between noncentrosymmetric and centrosymmetric materials.

TG-DTA analysis was performed on some members of the synthesized family from room temperature to 1100 K to verify stoichiometry and has showed close to 100% ion exchange between Na and H ions during synthesis (results are in Figure S1) and the pattern of decomposition at high temperature for these compounds. For this, a Rigaku Thermoplus EVO2 system was used in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Stable Structure Search by First-Principles Phonon Calculations. At the beginning, first-principles phonon calculations were performed to get an insight into the crystal structures of HRTiO₄. Although HRTiO₄ with R = Nd, Sm, Eu, Gd, and Dy was synthesized and investigated experimentally in this work, our calculations were done for HLaTiO₄ and HYTiO₄; because of the simplicity of their electronic structure, they have no 4f electrons, while the synthesized compounds have partially occupied 4f states. As revealed in our previous work, ^{12,13} the structural properties of the Na and Li families are sensitive not to the localized 4f electrons but to the ionic size of the rare earth ions. We suppose that the calculated structural properties of HLaTiO₄ and HYTiO₄ are considered as those corresponding to larger and smaller rare earth sides, respectively.

The calculated family tree diagram of HLaTiO₄ is presented in Figure S2, in which the total energy and space group of parent and child structures are shown. In the stable structure search starting from the parent RP P4/nmm structure, we found 27 kinds of more stable crystal structures including dynamically stable and unstable structures. All the structures could be divided into three different groups in terms of their structural features. Representative structures of the three groups (P4/nmm, Cm2e, and Pmnb for Groups 1, 2, and 3, respectively) are depicted in Figure 2a-c. Figure 2f plots the total energies of the structures of Groups 1-3 relative to that of the parent structure. Group 1 corresponds to the parent RP P4/nmm structure with the HO rocksalt layers (Figure 2a), in which the apical oxide ions are not on an extension of the hydroxyl bonds in the neighboring perovskite layers, preventing the formation of hydrogen bonding. In the structures of Group 2 (Figure 2b), hydrogen positions are optimized, resulting in the energetically favored directions of the hydroxyl bonds and/or the formation of hydrogen bonding and, hence, the energy gain with a width of -115 to -214 meV/f.u. The wide distribution of the total energy for Group 2 observed in Figure 2f manifests itself into a wide variety of possible hydrogen positions. The Group 2 structures are considered as structures constructed by removing hydrogen atoms from the Wyckoff sites 2c of the parent RP P4/nmm structure and placing hydrogen atoms at one-eighth of the 16k sites in its supercells. It is the P4/ nmm with the hydrogen randomly distributed at the 16k sites that has been reported experimentally so far.²³ The hydrogen atoms form hydroxyl bonds (solid lines) to the nearest neighbor oxide ions (\sim 1.0 Å) and hydrogen bonds (dashed lines) to the next nearest neighbor oxide ions (2.0 to 2.5 Å) in all the structures of Group 2, which is consistent with the fact that typical lengths of hydroxyl and hydrogen bonds are 0.96 to 0.98 Å and 2.2 to 2.5 Å, respectively.

As shown in Figure 2c, Group 3 consists of crystal structures whose layer-stacking patterns are different from those of Group 2. Focusing on the dotted rectangles in Figure 2b,c, one can see that a combined unit of perovskite—rocksalt—perovskite blocks is shifted to the [100] direction by half the in-plane lattice parameter $(1/2a_p$ in Figure 2b) of the parent structure. Consequently, the apexes of the oxygen octahedra surrounding Ti ions are vertically aligned at the proton layers when seen from

the [010] direction of the parent structure, while the apexes of the octahedra are not vertically aligned for Groups 1 and 2 when seen from neither the [100] or [010] direction. In Figure 3, we



Figure 3. Enlarged view of the perovskite blocks sandwiching the hydrogen blocks in the (a) Cm2e (Group 2) and (b) Pmnb (Group 3) structures. Only relevant units are illustrated. The solid and dashed lines between oxide ions and hydrogen atoms represent hydroxyl and hydrogen bonds, respectively. The colored planes are drawn to highlight the positional relationship between the perovskite blocks.

show an enlarged view of the perovskite blocks sandwiching the proton layer in the *Cm2e* (Group 2) and *Pmnb* (Group 3) structures to see how the hydrogen bonding is changed in the sliding. This clearly reveals that the hydrogen bond length becomes much shorter (~1.4 Å) after the sliding while the length of hydroxyl bonds is kept (~1.0 Å), indicating more effective hydrogen bonds compared to those of Group 2 structures. There are two structures in Group 3, and their total energies are identical (-298 meV). These structures were found to be dynamically stable. They are the most stable structures for HLaTiO₄. This kind of sliding has not been reported for HLaTiO₄ so far. Thus, our first-principles calculations predict that the layer sliding at the proton layers is driven by the formation of more effective hydrogen bonding for HLaTiO₄, that is, the large rare earth extremely.

On the other hand, in the stable-structure search for $HYTiO_4$, we found 128 structures that are more stable than the RP P4/ nmm structure. These could be categorized into five different groups including two additional groups along with Groups 1-3mentioned above for HLaTiO₄. The family tree diagram is illustrated for HYTiO₄ in Figure S3. Figure 2d,e shows representative structures belonging to the two additional groups, Groups 4 and 5, respectively. The total energies of the crystal structures are plotted in Figure 2g. As a general structural feature, the length of hydroxyl bonds is \sim 1.0 Å. The total energies of Group 2 for HYTiO₄ are distributed in the range from -53 to -159 meV/f.u, which is higher than that for HLaTiO₄. The hydroxyl and hydrogen bond lengths of Group 2 for HYTiO₄ are comparable to those for HLaTiO₄. The two structures of Group 3 observed for HLaTiO₄ were also seen for HYTiO₄. Both the total energies of the two structures for HYTiO₄ are -274 meV/ f.u., which are comparable to those for HLaTiO₄ (-298 meV/f.u.). Another structure of Group 3 was present with a total energy of -350 meV/f.u. for HYTiO₄. This structure encompasses significant distortions of the TiO₆ octahedra as well as the sliding, leading to a larger energy gain. Because of the small size of Y ions, OORs could occur so that the coordination environment of the Y ions surrounded by oxide ions is optimized with the coordination number and the Y-O bond length reduced, which could lead to a wider variety of structures compared to HLaTiO₄. Indeed, a lot of crystal structures with the OORs are found in the stable structure search for HYTiO₄. We

obtained the structures with only the OORs (without the sliding) as Group 4 and those with both the OORs and sliding as Group 5. As representative crystal structures for Groups 4 and 5, $P\overline{4}2_1m$ and P21 are illustrated in Figure 2d,e, respectively. The total energies of Groups 4 and 5 range from -68 to -300 meV/f.u. and -255 to -358 meV/f.u., respectively, depending on the patterns of OORs, the hydrogen atoms' positions, and their combinations. The minimum total-energy structure belongs to Group 5. Moreover, the OOR patterns of both the groups could be categorized into four types: $a^-a^-c^0$, $a^-b^-c^0$, $a^-b^0c^0/b^0a^-c^0$, and $2(a^{-}b^{0}c^{0})/2(b^{0}a^{-}c^{0})$. The $P\overline{4}2_{1}m$ structure illustrated in Figure 2d has the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ -type of OORs. The other OORs patterns are schematically shown in Figure S4, and the total energies for the OOR patterns are also plotted in Figure S5. For Group 4, the lowest total energy was obtained for the structures with the $a^-b^0c^0/b^0a^-c^0$ and $2(a^-b^0c^0)/2(b^0a^-c^0)$ -types of OORs, the former of which gives the most stable structures for NaRTiO₄ and LiRTiO₄. For Group 5, one of the structures with the $a^-b^0c^0/$ $b^0 a^- c^0$ -type of OORs has the lowest total energy, and the lowest energy for the $2(a^{-}b^{0}c^{0})/2(b^{0}a^{-}c^{0})$ -type of OORs is comparable to that for the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ -type. On the other hand, in contrast to Group 3, there are three additional patterns of the layer sliding. The details of the sliding patterns are described in Figure S6, and the total energies for the various OOR and layer-sliding patterns are shown in Figure S5. Among the structures with the various kinds of OORs and layer sliding, the lowest total-energy structure exhibits the $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ -type of OORs and the same sliding pattern as that for Group 3, as shown in Figure 2e. Thus, our firstprinciples calculations suggest that, for HYTiO₄, that is, the small rare earth limit side, the OORs and layer sliding reduce the total energies, and the largest energy gain was obtained by a concurrence of them.

In the following sections, we will present the results of Rietveld refinements for the SXRD patterns performed with an aid of the calculation results. As a result, we experimentally observe phase transitions relevant to the layer sliding, i.e., those from Groups 2 to 3, at low temperatures for HNdTiO₄ and HSmTiO₄, which have relatively larger rare earth ions, as predicted by our first-principles calculations. On the other hand, the layer sliding was not observed down to 80 K for HRTiO₄ with R = Eu, Gd, and Dy, which are relatively smaller; instead, we observed an $a^{-}b^{0}c^{0}/b^{0}a^{-}c^{0}$ -type of OORs and identified their structures as those corresponding to Group 4.

3.2. Detection of Noncentrosymmetricity by Optical Second Harmonic Generation. We performed optical SHG experiments on the HRTiO₄ compounds in order to see if these are noncentrosymmetric or not. The temperature dependence of the SHG intensity of HRTiO₄ (R = Dy, Gd, Eu, Sm, and Nd) is shown in Figure 4. All five compounds showed SHG signals, but



Figure 4. Optical second harmonic generation (SHG) vs temperature of HRTiO₄ for R = Eu, Gd, Dy, Sm, and Nd. The green region highlights the decomposition (dehydration) of the compounds.

we observed an order of magnitude difference in intensities between the HRTiO₄ (R = Dy, Gd, and Eu) and HRTiO₄ (R = Sm and Nd) compounds at 10 K. This strong SHG intensity for R = Dy, Gd, and Eu at 10 K, which monotonically decreases with increasing temperature, suggests a decreasing order parameter relevant to the noncentrosymmetric-to-centrosymmetric phase transition. The slope of the decreasing SHG signal changes at ~375 K for HEuTiO₄, ~500 K for HGdTiO₄, and ~620 K for HDyTiO₄, which are the noncentrosymmetric-to-centrosymmetric phase transition temperatures (T_{nc-c}) . Smaller rare earth ions lead to a greater driving force for an increase in OOR angles and, hence, a higher T_{nc-c} as observed in the ARTiO₄ (A = Na and Li) family of compounds reported before. In the case of HEuTiO₄, we observe a steady low intensity SHG signal above 375 K, which exists until about 500 K. This is likely due to the oriented OH dipoles that are present in the OH layer, which are also expected to be SHG active. For HEuTiO₄ and HGdTiO₄, we observe that the SHG intensity fluctuates in the temperature range of 550 to 750 K. This is due to SHG signal from the decomposition (dehydration) of HRTiO₄, which leads to the formation of defective metastable $R_{2-x} \prod_{y} Ti_2 O_7$ phases, which on further heating become pyrochlore R₂Ti₂O₇ compounds that have been reported before by Silyukov et al.²⁶ and Thangadurai et al.⁴³ For HDyTiO₄, the decomposition starts at slightly higher temperature (around 600 K) and hence the SHG signal starts fluctuating around that temperature. The SHG signal above \sim 550-600 K is therefore not interpretable in the context of HRTiO₄ phases. In the case of HNdTiO₄ and HSmTiO₄, the SHG signal is an order smaller than that of HRTiO₄ (R = Eu, Gd, and Dy) at 10 K and changes nonmonotonically, fluctuating throughout the temperature range of the experiment as we heat the sample to 800 K, indicating dynamically changing defects as the source of this signal, as well as oriented OH dipoles that form in the OH layer at all temperatures. These defects could be created when the layer sliding predicted by our DFT calculations occurs incoherently in a single grain below room temperature, as discussed later in Section 3.4. Beyond 600 K, all of these samples begin to dehydrate and decompose.

Thus, this experiment gives insight into the crystal structures of the HRTiO₄. The temperature-dependent SHG strongly indicates that HRTiO₄ (R = Eu, Gd, and Dy) undergoes centrosymmetric to noncentrosymmetric phase transitions between 300 and 600 K, whereas HRTiO₄ (R = Nd and Sm) remains centrosymmetric throughout this temperature range.

3.3. HRTiO₄ (R = Eu, Gd, and Dy) Structures Determined by Synchrotron X-ray Diffraction. Following the SHG experimental results, temperature-dependent synchrotron Xray diffraction (SXRD) experiments were performed on polycrystalline samples of HRTiO₄ in order to determine their crystal structures. All the temperature-variable diffraction patterns are presented in Figures S7 and S8. First, the SXRD patterns for $HRTiO_4$ with R = Eu and Gd at 500 K fit well using the tetragonal structural model with a P4/nmm space group.^{24,2} The high-temperature phase of these compounds is identified as the P4/nmm phases, which has been reported to be an RT phase of HRTiO₄ with R = La and Nd.²¹ As for HDyTiO₄, we cannot observe the high-temperature phase up to 500 K. On decreasing temperature, additional reflection peaks are observed around 1/d= 0.21 Å⁻¹ below 350 and 475 K for HRTiO₄ with R = Eu and Gd, respectively, as shown in Figure S9. Upon indexing the RT SXRD patterns of HRTiO₄ (R = Eu, Gd, and Dy) with respect to the tetragonal P4/nmm space group, these peaks are found to be a 1/2 1/2 1 superlattice reflection. The superlattice peak indicates the $\sqrt{2} \times \sqrt{2} \times 1$ -unit cell doubling of the P4/nmm structure due to a Brillouin zone boundary structural phase transition. Similar behavior has been observed for LiRTiO₄¹³ and NaRTiO₄,¹² which undergo a P4/nmm-to- $P\overline{4}2_1m$ phase transition due to the $a^-b^0c^0/b^0a^-c^0$ -type of OORs about the two axes perpendicular to the crystallographic *c*-axis (the 4-fold rotation axis). Our DFT calculations also suggest that a significant energy gain is caused by the $a^-b^0c^0/b^0a^-c^0$ -type of OOR. Therefore, the $P\overline{4}2_1m$ phase is considered as one of the plausible structures. As in the case of HYTiO₄, Nishimoto et al.²³ have previously reported a $P2_1/c$ monoclinic structure. In order to confirm the crystal structure for all the three HRTiO₄ compounds (R = Eu, Gd, and Dy), we first tried Miller indexing (Figure 5a shows



Figure 5. (a) SXRD refined pattern of HGdTiO₄ taken at 300 K. (b) Temperature-dependent lattice parameters of the HGdTiO₄ compounds. (c) Temperature dependence of the OOR angle, (d) area of the 1/21/21 superlattice peak with respect to P4/nmm, Δu_x (rare earth displacement), and (e) SHG intensity (compared with Δu_x^4) for HGdTiO₄.

indexing of $P\overline{4}2_1m$) and then refined the RT SXRD patterns by Rietveld analysis with $P\overline{4}2_1m$ as well as $P2_1/c$ models to find the best fit. The refinement involved all atoms except the hydrogen atom since X-ray diffraction is not sensitive to the hydrogen positions. We found that $P\overline{4}2_1m$ gives a slightly better fit than the $P2_1/c$ structure, as evidenced from comparison of the reliability indices, R_{wp} (reliability weighted pattern), and *S* (goodness of fit indicator) for the two models (Figure S7). We observed that R_{wp} and *S* differ by only a few decimal points. Figure 5a shows the indexed and refined SXRD pattern of HGdTiO₄ at 300 K. Using the $P\overline{4}2_1m$ model, we found $R_{wp} = 12.98\%$ and S = 1.89, whereas for $P2_1/c$, $R_{wp} = 13.45\%$ and S = 1.96. Hence, if we consider the SXRD refinement alone, it would be difficult to unambiguously determine the crystal structure of HRTiO₄ (R = Eu, Gd, and Dy). However, since HRTiO₄ (R = Eu, Gd, and Dy) is SHG active at room temperature, we can state that $P\overline{4}2_1m$ is likely to be the crystal structure. In addition, in the refined $P2_1/c$ structures (Table 1), we found that the short axes (b and c) are an exact match with each other to the second decimal place for all the three compounds and that all the interfacial angles among the three axes are almost 90°. These results clearly suggest that tetragonality is favored by the refinement. Even when a monoclinic $(P2_1/c)$ model is used, the lattice parameters and interfacial angles are close to those of tetragonal crystal structures within the uncertainty in the lattice parameters. After ascertaining the RT structure $(P\overline{4}2_1m)$ for the HRTiO₄ (R = Eu, Gd, and Dy) compounds, we turn to the temperature dependence of this structure. Temperature-dependent SXRD patterns of HGdTiO₄ were refined in the $P\overline{4}2_1m$ space group over the 90 to 475 K temperature range where we observe the 011 reflection, which corresponds to the 1/21/21 superlattice reflection of the P4/nmm structure. Around 500 K, the 011 reflection vanishes indicating that no OOR is present above this temperature. In this temperature range, we find a good match for the P4/nmm structure with reliability factors of $R_{wp} = 14.2$, $R_p =$ 11.35, and S = 1.62. The lattice parameters derived from the refined data between 90 and 500 K are shown in Figure 4b, highlighting the increase in lattice parameters (a and c) with increasing temperature. At 500 K, the $\sqrt{2} a$ and c of the refined P4/nmm unit cell are plotted to show a gradual change around this temperature, indicating a second-order phase transition. The gradual change in the shape of the superlattice peak (Figure S3) with temperature also supports this assertion. For HGdTiO₄ and HEuTiO₄, we can clearly trace the presence of the 011 $P\overline{4}2_1m$ reflection up to temperatures of ~475 and ~350 K, respectively, as shown in Figure S3. For HDyTiO₄, this peak is visible up to the highest experimental temperature of 475 K and is expected to exist up to ~600 K, as suggested by SHG measurements, as discussed above.

The temperature-dependent changes of the important structural parameters for HGdTiO₄ are shown in Figure 5c–e. These parameters are the OOR angle, $\theta_{\rm H}$ and $\theta_{\rm R}$ (illustrated in the inset of Figure 5c; derived from the refinement of the SXRD patterns in the $P\overline{4}2_1m$ model) in Figure 5c, the displacement of the Gd³⁺ ion denoted by Δu_x (the difference between the x fractional coordinates of Gd³⁺ ion in the $P\overline{4}2_1m$ and in the $\sqrt{2} \times \sqrt{2} \times 1$ cell doubled P4/nmm structures), and the area of the 011 reflection peak, in Figure 5d. The temperature dependence of the structural parameters indicates a change in the crystal structure of HGdTiO₄. The value of Δu_x and the area of the superlattice peak exhibit a systematic change with temperature, but this has not been confirmed for the OOR angle because of the difficulty of refining the oxygen atom positions. Both Δu_x and the 011 peak area decrease with increasing temperature as in the case of

Table 1. Comparison of Lattice Parameters between $P2_1/c$ and $P\overline{4}2_1m$ Structures for HRTiO₄ (R = Dy, Gd, and Eu)

	P21/c				$P\overline{4}2_1m$	
	a (Å)	b (Å)	c (Å)	β (deg.)	a (Å)	c (Å)
$HDyTiO_4$	11.5206 (01)	5.25897(06)	5.25775 (04)	90.0125(05)	5.25870(05)	11.5204(12)
HGdTiO ₄	11.7841(08)	5.2343(14)	5.23382(13)	89.9635(15)	5.2336(04)	11.7825(10)
HEuTiO ₄	11.8990(05)	5.2215(19)	5.22131(18)	89.9633(10)	5.2216(03)	11.89911(08)

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Figure 6. SXRD patterns of HSmTiO₄ at (a) 298 K, (b) 200 K, and (c) 90 K. Schematics showing the perovskite layer stacking of (d) *P4/nmm* and (e) *Cmcm* structures. In (f), schematic of defects created when the proton layer sliding occurs from opposing directions in the same layer. The thickness of the region of the defect is arbitrary. In (g), schematic of the four invariant directions of the layer sliding with respect to the 4-fold axis of the high symmetry *P4/nmm* unit cell is shown. In (h), the full width at half maximum of (*hkl*) planes that have plane normals nonorthogonal (blue stars) and orthogonal (red stars) to the (100) plane in the *Cmcm* unit cell is plotted against the 2 θ angle. In (i), the angles between the (*hkl*) plane normals and (100) plane normal in *Cmcm* unit cell are plotted against 2 θ .

NaRTiO₄ and LiRTiO₄ reported previously.^{12,13} These trends combined with the decreasing SHG intensity with increasing temperature mean that the degree of noncentrosymmetricity of the $P\overline{42}_1m$ phase decreases as temperature increases, eventually leading to a transition to the centrosymmetric P4/nmm phase. Δu_x is supposed to be proportional to an order parameter of the P4/nmm to $P\overline{42}_1m$ phase transition.¹² The value of Δu_x^4 is proportional to the SHG intensity of HGdTiO₄ up to ~280 K (Figure 5e), as has been supported by the Landau theory for NaRTiO₄ and LiRTiO₄.^{12,13} A deviation from this proportionality beyond 280 K is likely due to the fact that the SHG activity at room temperature and above is not solely dominated by the displacement of the Gd³⁺; instead, the SHG activity from the oriented OH dipoles provides additional contributions to SHG intensity in the HRTiO₄ (R = Eu, Gd, and Dy) compounds. The position of hydrogen atoms cannot be determined on the basis of our experimental results neither for the *P*4/*nmm* nor for the $P\overline{4}2_1m$ structures because of a poor sensibility of X-ray to hydrogen atoms. However, our DFT calculations for HYTiO₄ hint at the hydrogen atoms' positions; hydrogen atoms can be placed at a diverse variety of possible sites keeping the length of the hydroxyl bonds around 1 Å. In Figure 1a,b, at a distance of 1 Å from oxide ions in the OH layers, hydrogen atoms are put at the Wyckoff sites 16k and 8f, which are the least symmetric sites (site symmetry 1) in the P4/nmm and $P\overline{42}_1m$ structures, respectively. The site occupations are 0.125 and 0.5 for the P4/nmm and $P\overline{42}_1m$ structures to maintain stoichiometry. The DFT calculations also predict the OORs plus the sliding of the perovskite—rocksalt—perovskite layers to reduce the total energy of HRTiO₄ with small rare earth ions. However, phase transitions relevant to the layer sliding were not observed down to 80 K. As we see in the next section, such phase transitions occur in HRTiO₄ with large rare earth ions.

3.4. Sliding at the Proton Layers in HRTiO₄ (R = Nd and Sm) Observed by Synchrotron X-ray Diffraction. So far, we have discussed the noncentrosymmetricity of HRTiO₄ (R = Eu, Gd, and Dy) compounds, involving the smallest of the rare earths studied. For larger rare earth ions (R = Nd and Sm), the secondorder phase transition from P4/nmm to $P\overline{4}2_1m$ does not occur. Rather, we observe a quite different type of phase transition. The change in the SXRD pattern of HSmTiO₄ from RT to 90 K is shown in Figure 6a–c. Upon indexing, we find that P4/nmm is a good fit for the RT SXRD pattern of HRTiO₄ (R = Nd and Sm; Figure 6a). The results of Rietveld refinement are shown in Figure S1. For HSmTiO₄, we observe a splitting of some of the existing peaks as well as the appearance of new peaks at ~200 K highlighted with green color in Figure 6b. At lower temperatures close to but below 200 K, the peaks corresponding to the P4/ nmm structure gradually disappear and the SXRD pattern is completely changed by 100 K (Figure S7). Orthorhombic lattice vectors with a doubled *c*-axis lattice parameter compared to that of the P4/nmm structure are required to index the lowtemperature SXRD patterns. In the SXRD pattern of HSmTiO₄ taken at 90 K, *hkl* reflections have nonzero intensity only for k + l= 2n, consistent with A-centering. As a subset of this selection rule, 00l reflections are observed only for l = 2n, and 0klreflections are observed only for k + l = 2n. Also, we observed hk0reflections for h = 2m and k = 2n. Thus, taking into account the centrosymmetricity of the compounds, we conclude that space group Amma (No. 63) is a good match for the extinction rules. A standard setting for the space group number is Cmcm. Miller indices for the Cmcm setting are given in Figure 6b,c. For HNdTiO₄, the coexistence of the P4/nmm and Cmcm phases is visible from 250 K and below. At about 90 K, the compound is completely transformed to the *Cmcm* phase.

From the DFT calculations for HLaTiO₄, a significant energy gain is predicted to be obtained by sliding of a combined unit of perovskite—rocksalt—perovskite blocks to the [100] direction for the P4/nmm structure by half the in-plane lattice parameter. Withdrawing hydrogen atoms from the P4/nmm structure and sliding the combined units, a structure with *Cmcm* symmetry is obtained. Both the structures in Group 3 for HLaTiO₄ are represented by putting hydrogen atoms at half the Wyckoff 8*f* sites in the supercells of the *Cmcm* structure. Figure 1c illustrates the *Cmcm* structure where the 8*f* sites are partially occupied to maintain stoichiometry.

The structural refinement of the 90 K XRD patterns of R = Nd and Sm, using the *Cmcm* model, is shown in Figure S7. The R_{wp} = 21.019 and S = 4.768 for HSmTiO₄, while R_{wp} = 21.392 and S = 5.307 for HNdTiO₄. These reliability factors are higher than that of the other refinements mentioned before. This is due to the difficulties in fitting arising from significant broadness of some peaks. It has been observed that some of the *hkl* peaks assigned to

the *Cmcm* phase (Figure 6b,c) are much *broader* as compared to other peaks in both HSmTiO₄ and HNdTiO₄. We discuss the peak broadening as being related to the layer sliding. First, if we consider a two-dimensional rendition of the layer stacking in the P4/nmm unit cell (Figure 6d), we see that the oxygen octahedra of one layer are not stacked directly (oxide ions of one layer align on oxide ions of the adjacent layer) on the oxygen octahedra of the adjacent layers. In the case of the Cmcm unit cell, in which the layers are parallel to the x-z plane and normal to the y axis, when viewed from the $[001]_{Cmcm}$ direction, the oxygen octahedra are stacked directly over each other in pairs at the proton layers (Figure 6e). The structural change from the P4/nmm to the Cmcm phases can be interpreted as the sliding of perovskiterocksalt-perovskite layers over one another by half the length of the unit cell in the $\langle 100 \rangle_{P4/nmm}$ direction at the proton layers. Here, since the high symmetry structure is *P4/nmm*, there is a 4fold axis parallel to the $[001]_{P4/nmm}$ axis. This makes it possible to have four invariant directions ($[100]_{P4/nmm}$, $[\overline{1}00]_{P4/nmm}$ $[010]_{P4/nmm}$, and $[0\overline{1}0]_{P4/nmm}$) in which the layer sliding can occur at the proton layers (Figure 6g). When the layer sliding occurs in opposite directions at the same proton layer, the ideal stacking sequence is hindered and a defect can be formed where disorder would exist (Figure 6f). Such defects are expected to exist in each single crystal (or grain) in a polycrystalline sample. In a single crystal, when a (*hkl*) plane interacts with such a defect, it can lead to a broadening in that peak due to the disorder. In Figure 6h, when the fwhm of all the major *hkl* reflections is plotted against 2θ , we make a striking observation: the 1*l*0 and 1*l*1 reflection peaks with l = 2n + 1 are broader than the 0*l*0 and 0l1 reflection peaks with l = 2n, respectively. We note next that the normals of the (0l0) and (0l1) planes with l = 2n are orthogonal to the (100) plane normal, which is the sliding direction (Figure 6i), meaning that these two planes are not affected by the layer sliding significantly. On the other hand, the plane normals of the 1*l*0 and 1*l*1 reflections with l = 2n + 1 make $<90^{\circ}$ angles with the (100) plane. Hence, these planes interact more strongly with some defects stemming from the layer sliding and thereby are observed to be broadened.

Thus, for R = Nd and Sm, the layer sliding occurs without any OOR, retaining centrosymmetricity. It is known that stacking patterns of perovskite layers depend on the ionic radius of cations. For example, there are a variety of stacking patterns in the ALaNb₂O₇ (A = H, Li, Na, K, Rb, and Cs) family, 44-46 which has double perovskite layers consisting of NbO₆ octahedra. For A = Li and Na, the structures have been found to be tetragonal with an I-type lattice. On the other hand, KLaNb₂O₇ has a basecentered orthorhombic lattice. When comparing ALaNb₂O₇ with A = K to that with A = Li and Na, the perovskite layers slide at the alkaline oxide layers in the directions of the $\langle 100 \rangle$ axes of the tetragonal lattice. When moving A = K to A = Rb and Cs, an additional layer sliding occurs in another tetragonal direction, making the perovskite layers align with the neighboring layers. As a result, $ALaNb_2O_7$ with A = Rb and Cs has a DJ structure. Also, the stacking pattern of perovskite layers is changed during an ion-⁷ The exchange reaction from NaEuTiO₄ to Ca_{0.5}EuTiO₄.⁴ former has a RP structure, while the latter has a combined structure of RP and DJ. HLaNb₂O₇ has the same type of perovskite layer stacking as that for A = Rb and Cs, although the configuration of the A cation is different. Interestingly, the layer stacking pattern in HLaNb₂O₇ is caused by hydrogen bonding in the proton layer as in the present HRTiO₄ system. The pattern of the layer stacking in HLaNb₂O₇ is different from that in HRTiO₄ due to a different number of hydrogen atoms per oxygen

octahedron at the proton layers. In these compounds, when the cations are changed, stacking patterns change at the cation layers. This is not the case for the present $HRTiO_4$ compounds. In the $HRTiO_4$ system, however, it depends on the rare earth size whether the layer sliding occurs at the proton layers or not. Furthermore, the phase transitions relevant to the layer sliding occur with changing temperature. From these viewpoints, we observed very intriguing phase transitions in the present system.

4. CONCLUSION

While all previous studies considered all HRTiO₄ compounds to be centrosymmetric, we have developed a comprehensive understanding of the crystal structure and phase transitions in the HRTiO₄ family, finding compounds in this family that are noncentrosymmetric. Figure 7 shows the complete phase



Figure 7. Phase diagram derived from SXRD data of $HRTiO_4$ (R = Nd, Sm, Eu, Gd and Dy). The yellow-orange shaded region between 250 and 100 °C indicates the coexistence of the *P4/nmm* and *Cmcm* phases in HNdTiO₄ and HSmTiO₄.

diagram of the HRTiO₄ family. HRTiO₄ (R = Eu, Gd, and Dy) compounds undergo a phase transition from P4/nmm to $P\overline{42}_1m$ above room temperature. On the other hand, $HRTiO_4$ (R = Nd and Sm) undergoes a phase transition from P4/nmm to Cmcm below room temperature. We have established that, for larger rare earth ions such as R = Nd and Sm, the octahedral rotation is absent, but in order to optimize the length and direction of hydrogen bonding, sliding of the perovskite-rocksalt-perovskite layers occurs, as shown in Figure 3. In the case of R = Eu, Gd, and Dy, there is no layer sliding as the environment around the hydrogen atoms is optimized by OORs. These observations indicate that OORs and layer sliding are competing phenomena that determine the presence or lack of inversion symmetry in this family of compounds. Besides establishing a new mechanism for noncentrosymmetricity, this finding in HRTiO₄ could have interesting consequences for anisotropic electronic and ionic conduction in this family of materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b04103.

Synchrotron X-ray patterns and refined structures; room temperature laboratory X-ray patterns; temperature dependence of superlattice peaks; comparison of Rietveld refined statistical indicators of different structures; TG-DTA data and analysis; family tree calculation of HRTiO₄ (R = La, Y) (PDF)

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Notes

The authors declare no competing financial interest.

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