

**High-pressure structural stability of multiferroic hexagonal  $RMnO_3$  ( $R = Y, Ho, Lu$ )**P. Gao,<sup>1</sup> Z. Chen,<sup>1</sup> T. A. Tyson,<sup>1,2</sup> T. Wu,<sup>1</sup> K. H. Ahn,<sup>1,2</sup> Z. Liu,<sup>3</sup> R. Tappero,<sup>4</sup> S. B. Kim,<sup>2</sup> and S.-W. Cheong<sup>2</sup><sup>1</sup>*Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, USA*<sup>2</sup>*Rutgers Center for Emergent Materials and Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*<sup>3</sup>*Geophysical Laboratory, Carnegie Institution of Washington, D.C. 20015, USA*<sup>4</sup>*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973, USA*

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Structural changes in  $RMnO_3$  ( $R = Y, Ho, Lu$ ) under high pressure were examined by synchrotron x-ray diffraction methods at room temperature. Compression occurs more readily in the  $ab$  plane than along the  $c$  axis. With increased pressure, a pressure-induced hexagonal to orthorhombic phase transition was observed starting at  $\sim 22$  GPa for  $Lu(Y)MnO_3$ . When the pressure is increased to 35 GPa, a small volume fraction of  $Lu(Y)MnO_3$  is converted to the orthorhombic phase and the orthorhombic phase is maintained on pressure release. High-pressure infrared absorption spectroscopy and Mn  $K$ -edge near-edge x-ray absorption spectroscopy confirm that the hexagonal  $P6_3cm$  structure is stable below  $\sim 20$  GPa and the environment around the Mn ion is not changed. Shifts in the unoccupied  $p$ -band density of states with pressure are observed in the Mn  $K$ -edge spectra. A schematic pressure-temperature phase diagram is given for the small ion  $RMnO_3$  system.

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**I. INTRODUCTION**

The rare-earth ( $R$ ) manganites (such as  $RMnO_3$ ,  $RMn_2O_5$ , and  $R_2Mn_2O_7$ ) are a group of systems with interesting properties which have attracted interest from the fundamental and basic physics perspectives.<sup>1</sup> The  $RMnO_3$  systems fall into two basic structures: hexagonal and orthorhombic phase depending on the ionic radius of  $r$ . Small ionic radius  $RMnO_3$  systems ( $R = Ho-Lu, Y$ ) are in the hexagonal structure and exhibit both ferroelectric and magnetic properties. The magnetic ordering temperature  $T_N$  is  $\sim 90$  K (Ref. 2) and the ferroelectric ordering temperature  $T_C$  is near  $\sim 900$  K. The low-high temperature phase transition is predicted to pass through several aristotype phases.<sup>3</sup> The hexagonal structure ( $P6_3cm, Z = 6$ ) is built up of  $MnO_5$  trigonal bipyramids, which are illustrated in Fig. 1. In the basal ( $ab$ ) plane, the pyramids are linked at the base corners to construct a triangular lattice. The  $R$  ions are located between these  $MnO_5$  layers and are linked with oxygen atoms. Each consecutive ( $ab$  plane) layer of  $MnO_3$  [Fig. 1(b)] is rotated by  $180^\circ$  about the  $c$  axis. They are geometrically frustrated antiferromagnetic materials.<sup>4</sup> The  $Mn^{3+}$  spins and the associated magnetic exchange are confined to the basal ( $ab$ ) plane, and the  $Mn^{3+}$  magnetic ground state produces a  $120^\circ$  angle between spins on local Mn triangles.

A first-order structural transition occurs near 1200 K on cooling from the high-temperature centrosymmetric  $P6_3mmc$  ( $Z = 2$ ) phase to an asymmetric low-temperature  $P6_3cm$  phase. The onset of the ferroelectricity with the spontaneous polarization  $P_s$  along the  $c$  axis<sup>5</sup> is observed to occur near  $T_C \sim 900$  K. If the high temperature is accompanied with high pressure ( $\sim 4$  GPa and  $\sim 1000$  °C),<sup>6-8</sup> the hexagonal (Hex) compound will be converted into a corresponding orthorhombic (Ortho) phase, which has a higher density and is strongly Jahn-Teller distorted.<sup>9</sup> By other techniques, such as chemical solution method<sup>10</sup> and epitaxial thin-film growth techniques<sup>11,12</sup> the orthorhombic compound also can be stabilized. On an appropriate perovskite substrate, the hexagonal  $RMnO_3$  is forced into the orthorhombic form.<sup>11</sup> In other words, substrate strain can stabilize the orthorhombic

phase for small size ions. Vice versa, a substrate such as  $ZrO_2$  ( $Y_2O_3$ ) (YSZ) can epitaxially grow Hex-Dy $MnO_3$  and Hex-Tb $MnO_3$  films, which are normally in the orthorhombic structure.<sup>12</sup> When the normal Hex- $RMnO_3$  films are deposited on the YSZ substrate, the lattice parameter  $c$  of the film in the out-of-plane direction is tuned by the film thicknesses.<sup>12</sup> If the cell is elongated along the  $c$  axis, it would enhance the spontaneous polarization value. In a relaxed Hex- $RMnO_3$  film, the  $T_N$  value is lower than the value of the bulk material.<sup>13</sup>

Under high-pressure conditions, the dielectric and magnetic properties of Hex- $RMnO_3$  have been studied<sup>14-18</sup> up to 6 GPa. In those works, the hexagonal structure is not changed.<sup>15,19</sup> The  $HoMnO_3$  spin rotation transition temperature ( $T_{SR}$ ) decreases linearly with applied pressure at a rate of  $dT_{SR}/dp = -2.05$  K/GPa.<sup>14</sup> The Mn magnetic moment is suppressed. At 10 K, the ordered magnetic moment values are reduced with rates  $dM/dP = -0.35$   $\mu B$  GPa<sup>-1</sup> in  $YMnO_3$  and  $-0.08$   $\mu B$  GPa<sup>-1</sup> in  $LuMnO_3$ .<sup>16,17</sup> The decrease in  $LuMnO_3$  is due to an enhancement of the geometrical frustration effects on the triangular lattice. At the same time, the magnetic symmetry of the triangular antiferromagnetic (AFM) state (the irreducible representation  $\Gamma_2$ ) remains unchanged. However, spin reorientation of Mn magnetic moments and a change in the symmetry of the AFM structure occur in  $YMnO_3$ . A spin-liquid state due to magnetic frustration on the triangular lattice forms by Mn ions at normal pressure and  $T > T_N = 70$  K, and an ordered triangular AFM state occurs with the symmetry of the irreducible representation  $\Gamma_1$  at  $T < T_N$ . The high-pressure effect leads to a spin reorientation of Mn magnetic moments and a change in the symmetry of the AFM structure, which can be described by a combination of the irreducible representations  $\Gamma_1$  and  $\Gamma_2$ .<sup>16-18</sup> High pressure induces a spin-liquid phase in  $YMnO_3$ , coexisting with the suppressed long-range AFM order. The spin-liquid phase exhibits temperature dependence distinctively different from short-range spin correlations seen at ambient pressure. Its formation occurs through an in-plane Mn-O bond symmetrization and results in reduced magnetoelastic coupling at high pressures.<sup>19</sup>

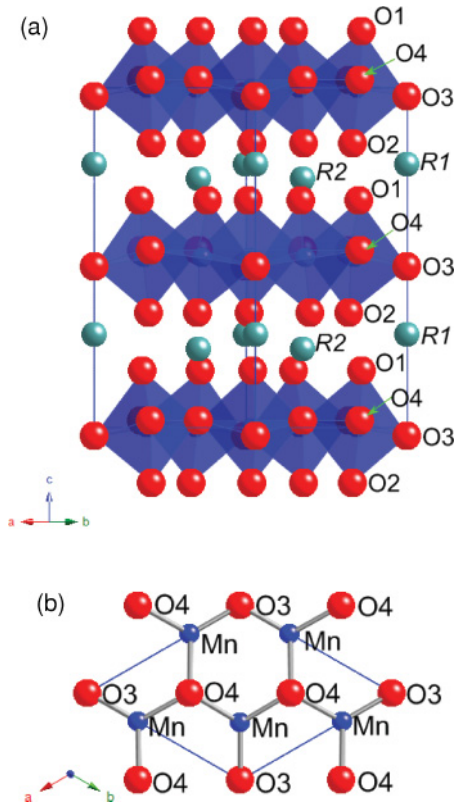


FIG. 1. (Color online) (a) The crystal structure of hexagonal  $RMnO_3$  showing the  $MnO_5$  bipyramids and (b) the triangular lattice of Mn ions linked by oxygen atoms.

Structurally, high-pressure Raman spectroscopy reveals the possibility of a hexagonal-orthorhombic phase transition happening at room temperature induced by pressure.<sup>20</sup> In  $Hex-Ho_{0.8}Dy_{0.2}MnO_3$ , the phase transition pressure is interpreted to occur at  $\sim 10$  GPa by observation of Raman phonon changes. No combined systematic study of the structure of  $Hex-RMnO_3$  under pressure has been conducted on this system to date.

In this work, we present the hydrostatic and quasihydrostatic pressure effects on  $RMnO_3$  ( $R = Y, Ho,$  and  $Lu$ ) to explore how the structural, vibrational, and optical properties change with pressure. To effect this, synchrotron-based x-ray diffraction (XRD), x-ray absorption spectroscopy (XAS), and infrared (IR) methods are utilized at room temperature (298 K). We find that, at room temperature, a pressure-induced hexagonal-orthorhombic phase transition requires a pressure above  $\sim 22$  GPa for  $Lu(Y)MnO_3$  and results in only a small fractional conversion of  $Lu(Y)MnO_3$  to the orthorhombic phase. The hexagonal  $RMnO_3$  is stable below this pressure. By checking the dipole moment of a unit cell, we find that the spontaneous polarization is a constant value under hydrostatic pressures at least up to  $\sim 11$  GPa where we have conducted detailed structural refinement. The IR absorption spectrum and x-ray near-edge absorption spectrum confirm that  $P6_3cm$  is a stable structure under  $\sim 20$  GPa and the environment around the Mn ion is not changed. The temperature for the transition to the orthorhombic phase is strongly suppressed by the application of pressure.

## II. EXPERIMENTAL AND COMPUTATIONAL METHODS

Finely ground  $RMnO_3$  polycrystalline powders made by the solid-state reaction method were sealed into a diamond anvil cell (DAC) with three to four ruby chips for pressure calibration. Monochromatic x-ray ( $\lambda = 0.4066$  Å) powder diffraction under high pressures was completed at the X17C beam line at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory. A charge-coupled device (Mar,  $2048 \times 2048$  pixels with  $80 \mu m$  resolution) was used to record the two dimensional (2D) diffraction rings. The integration of the data to yield intensity vs  $2\theta$  diagrams was conducted by the program FIT2D.<sup>21</sup> A methanol/ethanol/water (16:3:1) mixture was used as the pressure medium in x-ray diffraction experiments whose glass transition pressure is  $\sim 10.5$  GPa.<sup>22</sup> The pressure-dependent synchrotron IR absorption spectra were measured at the U2A beam line at NSLS. A vacuum infrared microscope provided a resolution of  $4 \text{ cm}^{-1}$  in far-IR ( $100\text{--}650 \text{ cm}^{-1}$ ) range. It was equipped with a  $3.5 \mu m$  Mylar beam splitter, a 40 mm working distant reflecting objective, and a Si bolometer detector. CsI was used to dilute the  $RMnO_3$  powder and acted as the pressure medium in IR absorption measurements. The pressures generated by DAC were calibrated by the ruby fluorescence method. The transmission mode x-ray absorption measurements were performed at beam line X27A at the Mn  $K$  edge in a DAC utilizing a pair of partially perforated diamond anvils. The pressure calibration was based on the compression curves<sup>23,24</sup> from the Fe x-ray absorption fine structure spectra of a thin Fe metal layer loaded in the cell with the sample.

To determine the nature of the fastest varying IR modes, the eigenvectors and eigenvalues of the dynamic matrix were calculated following the approach taken previously in  $HoMnO_3$ .<sup>25</sup> The structure as a function of pressure was simulated in the density functional calculations using the projector augmented wave approach<sup>26</sup> for  $YMnO_3$  and  $LuMnO_3$  (with no open  $Rf$  shells).

## III. RESULTS AND DISCUSSION

Diffraction patterns of  $RMnO_3$  are shown in Fig. 2(a) for the pressure range up to  $\sim 17$  GPa. At ambient pressure, three hexagonal phases show similar diffraction patterns. The lattice parameters ( $a$  and  $c$ ) are  $a = 6.1151$  Å,  $c = 11.3781$  Å ( $YMnO_3$ );  $a = 6.1345$  Å,  $c = 11.4179$  Å ( $HoMnO_3$ ); and  $a = 6.0485$  Å,  $c = 11.3830$  Å ( $LuMnO_3$ ) at ambient pressure and were extracted by the Rietveld method.<sup>27</sup> These values agree with the published results<sup>7</sup> ( $YMnO_3$ ,  $a = 6.14666$  Å and  $c = 11.4411$  Å;  $HoMnO_3$ ,  $a = 6.13820$  Å and  $c = 11.4118$  Å; and  $LuMnO_3$ ,  $a = 6.03011$  Å and  $c = 11.3648$  Å). When the crystal cell is compressed, the diffraction peaks shift toward high  $2\theta$  value and the peak intensities are varied as expected. It is a continuous process with no additional peaks appearing in this pressure range (up to  $\sim 17$  GPa in the figure). Pressure dependence of the volume was fit by the Murnaghan equation of state:  $V(P) = V_0[1 + B'_0(P/B_0)]^{-1/B'_0}$ , where  $V_0$ ,  $B_0$ , and  $B'_0$  are the volume for a solid, the zero pressure bulk modulus, and the bulk modulus pressure derivative. In the hexagonal phase, the  $B_0$  values are  $112 \pm 8$  GPa ( $YMnO_3$ ),  $130 \pm 7$  GPa ( $HoMnO_3$ ),

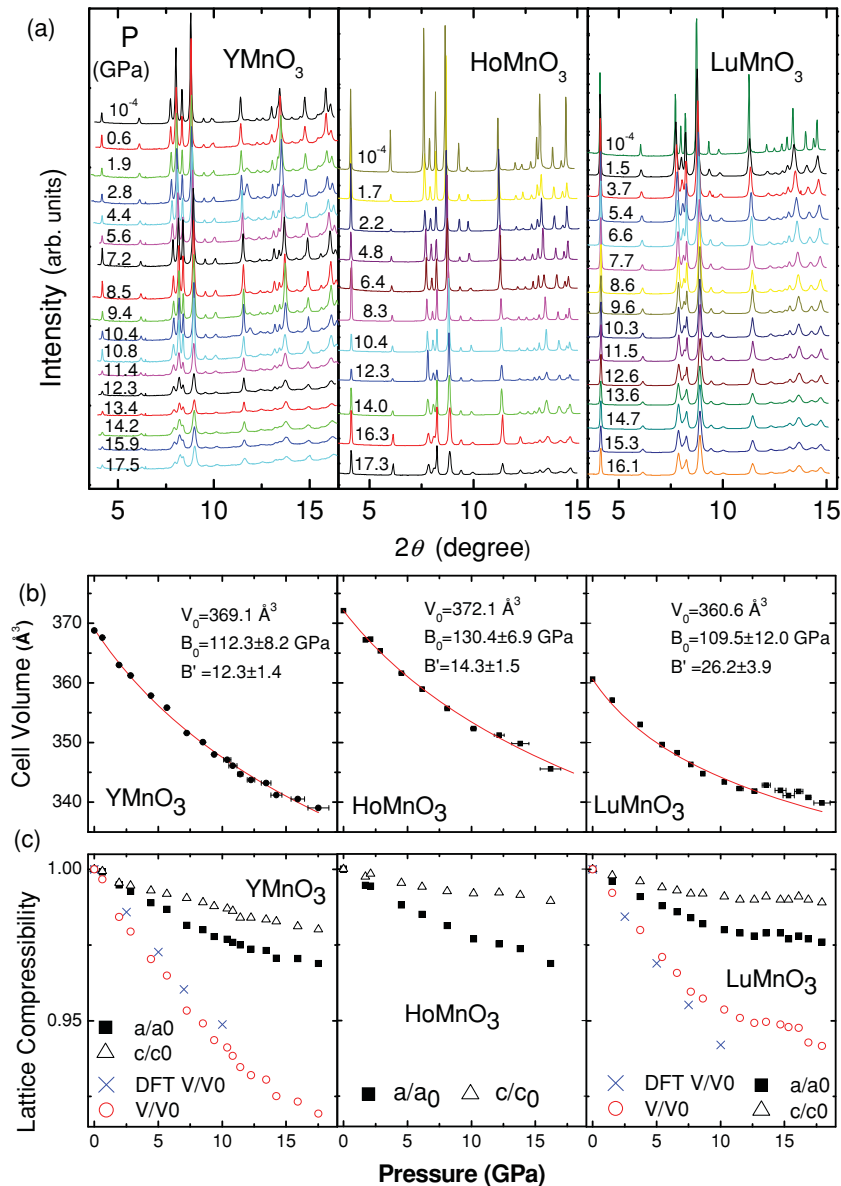


FIG. 2. (Color online) (a) X-ray powder diffraction patterns of  $\text{RMnO}_3$  at various pressures ( $T = 298$  K). From left panel to right panel are diffraction patterns of  $\text{YMnO}_3$ ,  $\text{HoMnO}_3$ , and  $\text{LuMnO}_3$ , respectively. (b) Pressure-dependent unit-cell volumes (dots) and the first-order Murnaghan fit (solid line). (c) Compressibility of lattice parameters of  $a$ ,  $c$ , and  $V$ . The crosses are from the DFT calculations. Note the higher compressibility of the  $a$  axis.

and  $109 \pm 12$  GPa ( $\text{LuMnO}_3$ ). For the typical Ortho- $\text{LaMnO}_3$ , the values of  $B_0$  and  $B'_0$  are  $108 \pm 2$  GPa and  $8.5 \pm 0.4$ , respectively.<sup>28</sup> The highly anisotropic compressibility of the  $P6_3cm$  structure is indicated by the  $B'_0$  values 12, 14, and 26, respectively, compared to the  $Pbnm$  orthorhombic structure. Figures 2(b) and 2(c) illustrate the pressure-dependent cell volume change and lattice  $a, c$  variations. In the  $ab$  plane, the cell is much easier to compress than along the  $c$  direction. The pressure-dependent variation of  $a$  is about twice the change for  $c$ . The volume and structural parameters of  $\text{YMnO}_3$  and  $\text{LuMnO}_3$  are calculated by the density functional theory (DFT) method. The DFT results show a coincidence with the experimental result on the pressure-dependent volume change. While the  $\text{YMnO}_3$  system is well matched by the model, the  $\text{LuMnO}_3$  with a closed  $4f$  shell is not well modeled.

By neutron diffraction, the structure under pressure has been determined up to 6 GPa.<sup>16,17</sup> Here it is found that the oxygen position parameters do not significantly vary with pressure. Moreover, for the general hexagonal ( $P6_3cm$ )  $\text{ABO}_3$  ( $A = R, B = \text{Mn, Fe, and Ga}$ ) system, replacement of the  $A$

and/or  $B$  site by ions of different radii does not significantly modify the atomic positions.<sup>8,29–31</sup> Mn is approximately in the center of its oxygen environment.<sup>32</sup> In the DFT simulations, the same trend is observed up to 10 GPa. The x-ray scattering factor of oxygen is small compared to  $R$  and Mn, so uncertainties will be high on the O atomic positions. Hence in our fitting process, the oxygen atoms are fixed and only the heavy metallic atomic positions ( $R$  and Mn) are adjusted. This assumption is justified by the above observations. Below 11 GPa, the structural fit shows that the atomic positions of Mn and  $R$  hold the original positions: R1 at  $2a$  ( $0,0,\sim 1/4$ ) and R2 at  $4b$  ( $1/3,-2/3,\sim 1/4$ ), and Mn at  $6c$  ( $\sim 1/3,0,\sim 0$ ), which is plotted in Fig. 3(a). By comparing the distances (below 11 GPa) between the Lu and Mn ions (Mn-Lu1 and Mn-Lu2 distances) in Fig. 3(b), we found that those values are conserved. This implies that the heavy atoms framework is unchanged (and the buckling of the layers is maintained at least up to 11 GPa); the oxygen atoms will be embedded into this framework as under normal pressure conditions. Beyond 11 GPa, an accurate Rietveld fit is not feasible due to distortion

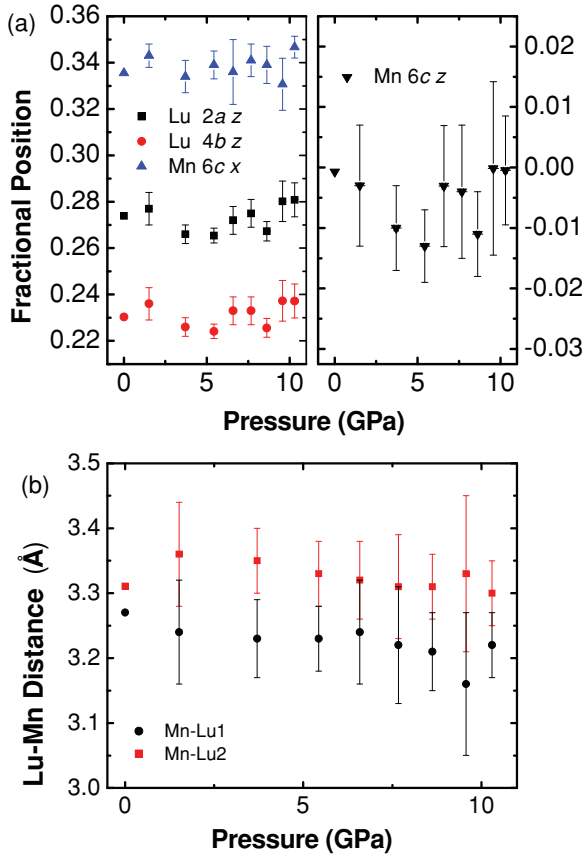


FIG. 3. (Color online) Pressure-dependent fractional positions of Lu1 2a (0,0,z), Lu2 at 4b (1/3,2/3,z), and Mn at 6c (x,0,z) in (a) and the distance between Mn and Lu ions in (b).

of the peak shapes by the glass transition of the pressure medium (nonhydrostatic conditions). However, the diffraction peak positions which determine the lattice parameters remain stable.

To further explore the pressure dependence at higher pressure, the pressure-dependent IR optical density (OD) spectra are conducted and displayed in Fig. 4(a)–4(c). The OD spectra of pure CsI have no significant change with the pressure increase (except the low-frequency  $\sim 100\text{ cm}^{-1}$  edge shift). Under the hydrostatic pressure condition, there is no abrupt profile shape change in the OD spectra. The phonons of the samples are hardening with pressures and the intensity is redistributed as expected. Natural DyMnO<sub>3</sub> is an orthorhombic phase and the OD spectrum is a typical example [Fig. 4(d)]. It is used as a reference to show that no conversion to this phase occurs up to  $\sim 20\text{ GPa}$ . No characteristic peaks in common were found between the Hex-RMnO<sub>3</sub> OD spectrum and the Ortho-DyMnO<sub>3</sub> OD spectrum. The spectrum shapes show a big difference in the region  $\sim 300\text{--}550\text{ cm}^{-1}$  for the Ortho and Hex phases because of the structure difference of bipyramidal (MnO<sub>5</sub>) and octahedral (MnO<sub>6</sub>). Up to  $\sim 20\text{ GPa}$ , both the OD spectra and the x-ray diffraction result show no phase transition and the crystal structure is slightly modified. The  $P6_3cm$  is a stable structure in this pressure range at room temperature. From that, we can deduce that in previous work of the synthesis of metastable orthorhombic materials,<sup>6–8</sup> the heat treatment plays the key role. With the thermal

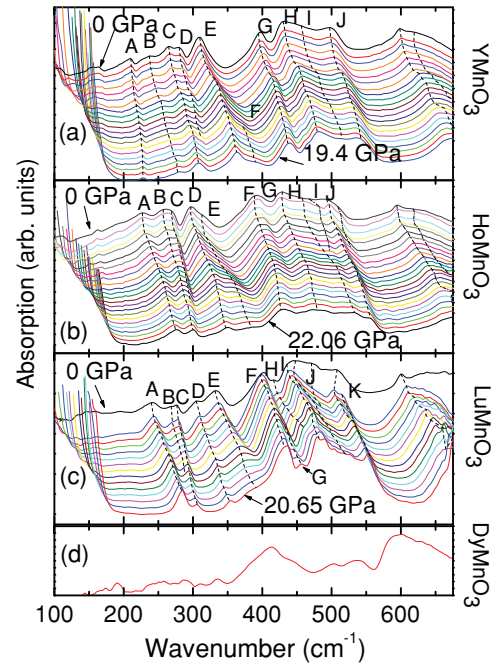


FIG. 4. (Color online) Pressure-dependent IR optical density spectrum of Hex-RMnO<sub>3</sub> at room temperature. (a) YMnO<sub>3</sub> IR absorption spectrum (pressure: 0.00, 0.58, 1.17, 2.01, 3.02, 3.96, 4.98, 7.11, 7.97, 8.74, 9.35, 10.04, 10.99, 11.94, 12.98, 14.03, 15.08, 16.04, 17.11, 18.07, and 19.40 GPa). (b) HoMnO<sub>3</sub> IR absorption spectrum (pressure: 0.00, 0.58, 1.08, 2.01, 3.19, 4.13, 5.23, 5.91, 7.03, 8.14, 9.00, 10.29, 11.07, 12.56, 13.33, 14.03, 15.61, 16.40, 17.10, 18.25, 19.22, 20.46, and 22.06 GPa). (c) LuMnO<sub>3</sub> IR absorption spectrum (pressure: 0.00, 1.74, 2.95, 4.16, 5.30, 6.64, 7.99, 9.26, 10.88, 12.37, 14.04, 15.24, 17.31, 18.69, and 20.65 GPa). (d) Ambient IR optical density spectra of orthorhombic DyMnO<sub>3</sub>.

treatment (the temperature  $\sim 1000\text{ K}$ ), the atoms acquire enough energy to overcome chemical barriers required to break bonds needed to construct a different symmetry under pressure ( $\sim 4\text{ GPa}$ ).

We now look in detail at the phonon pressure dependence. By group theory analysis, Hex-RMnO<sub>3</sub> has been reported to have 23 IR-active phonon modes ( $9A_1 + 14E_1$ ).<sup>33</sup> In our work, the ambient RMnO<sub>3</sub> absorption spectrum shapes agree with the published results of YMnO<sub>3</sub>.<sup>33</sup> Eleven Lorentzian oscillators<sup>33</sup> can index our ambient YMnO<sub>3</sub> OD spectrum well. The phonon assignments are listed in Table I and compared to the measurements of Ref. 33. The profiles are maintained for all IR pressures studied as pressure increases up to  $\sim 20\text{ GPa}$ . However, the asymmetry in compressibility in the *ab* plane vs the *c* direction plays an important role in this variation between different phonons. Phonons shift to higher frequencies with differing rates resulting in pressure-dependent changes in peak separation or even merger at specific pressures. For the YMnO<sub>3</sub> sample, at  $\sim 12\text{ GPa}$ , a weak phonon  $\sim 375\text{ cm}^{-1}$  (labeled *F*) is separated from the phonon  $\sim 351\text{ cm}^{-1}$  which is the ambient pressure phonon  $\sim 310\text{ cm}^{-1}$  (symmetry  $E_1$ , labeled *E*), and the ambient pressure absorption lines of  $265\text{ cm}^{-1}$  ( $A_1$ , labeled *C*) and  $281\text{ cm}^{-1}$  ( $E_1$ , labeled *D*) merge into one  $301\text{ cm}^{-1}$  at  $\sim 14\text{ GPa}$ . The OD spectra of Hex-HoMnO<sub>3</sub> and Hex-LuMnO<sub>3</sub> show more than 11 IR phonons at ambient pressure. In Fig. 4(b)

TABLE I. IR phonons of Hex- $RMnO_3$  ( $R = Y, Ho,$  and  $Lu$ ) at the ambient condition.

This work			YMnO3 from Iliev (Ref. 33)		
YMnO <sub>3</sub>	HoMnO <sub>3</sub>	LuMnO <sub>3</sub>	Expt. (cm <sup>-1</sup> )	Mode symmetry	Direction and sign of the largest atomic displacements
264.9	269.2	276.8	265	<i>A1</i>	+z( <i>R/Y1, R/Y2</i> ), -z( <i>Mn</i> )
394.4	389.9	398.7	398	<i>A1</i>	+z( <i>O3</i> ), +z( <i>O4</i> ), +x, y( <i>O2</i> ), -x, y( <i>O1</i> )
430.2	426.4	435.2	428	<i>A1</i>	+z( <i>O4,O3</i> ), -z( <i>Mn</i> )
	467.6			<i>A1</i>	+x, y( <i>O1,O2</i> ), -x, y( <i>Mn</i> )
619.1	614.5		612	<i>A1</i>	+z( <i>O1,O2</i> ), -z( <i>Mn</i> )
210.5	226.6	240.0	211	<i>E1</i>	+x, y( <i>O1,O2</i> ), -x, y( <i>R/Y1,R/Y2</i> )
237.0	257.1	268.5	238	<i>E1</i>	x,y( <i>Mn,O3</i> ), z( <i>O1,O2</i> )
280.2	296.7	304.7	281	<i>E1</i>	+x, y( <i>O1,O2</i> ), -x, y( <i>O3</i> )
309.6	313.1	331.8	308	<i>E1</i>	+x, y( <i>O1,O2,O3</i> ), -x, y( <i>O4,Mn</i> )
		416.3		<i>E1</i>	+x, y( <i>O1</i> ), -x, y( <i>O2</i> )
		447.7		<i>E1</i>	+x, y( <i>O1</i> ), -x, y( <i>O2</i> )
456.1	457.6	470.9	457	<i>E1</i>	+x, y( <i>O4,O3</i> ), -x, y( <i>O2,O1,Mn</i> )
497.1	492.3	507.8	491	<i>E1</i>	+x,y( <i>O4,O3,O1,O2</i> ),-x, y( <i>Mn</i> )
	508.9			<i>E1</i>	x, y( <i>O4</i> )
598.1	594.3	599.8	596	<i>E1</i>	x, y( <i>O3</i> )

of the HoMnO<sub>3</sub> OD spectra, phonons ~468 cm<sup>-1</sup> (labeled I) and ~509 cm<sup>-1</sup> (labeled J) are indexed at ambient pressure. At ~10 GPa, the phonon ~457 cm<sup>-1</sup> (labeled H) merges into the phonon ~468 cm<sup>-1</sup> (label I); phonons ~492 and ~509 cm<sup>-1</sup> (near J) become one. When the pressure reaches ~16.5 GPa, two phonons with energy 256 (ambient, label B) and 268 cm<sup>-1</sup> (ambient, label C) merge. In Fig. 4(c) of the LuMnO<sub>3</sub> sample, weak vibrations with a maximum at ~416 cm<sup>-1</sup> (labeled H) and ~447 (near label I) and 515 cm<sup>-1</sup> (~1.74 GPa, labeled K) can be found. Phonons ~503 (~1.74 GPa) and ~515 cm<sup>-1</sup> (label K) become one again at ~10.9 GPa. Near ~14.6 GPa, the ambient vibrations 268 (labeled B) and 286 cm<sup>-1</sup> (labeled C) are merging into ~293 cm<sup>-1</sup>. The phonon with a frequency

~400 cm<sup>-1</sup> (ambient, labeled F) is two phonons ~432 and ~456 cm<sup>-1</sup> (labeled G) at ~20.5 GPa.

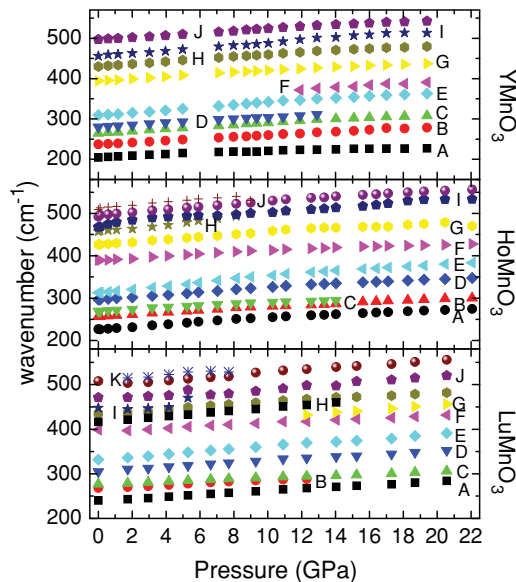


FIG. 5. (Color online) Pressure-dependent phonon frequencies of YMnO<sub>3</sub>, HoMnO<sub>3</sub>, and LuMnO<sub>3</sub>.

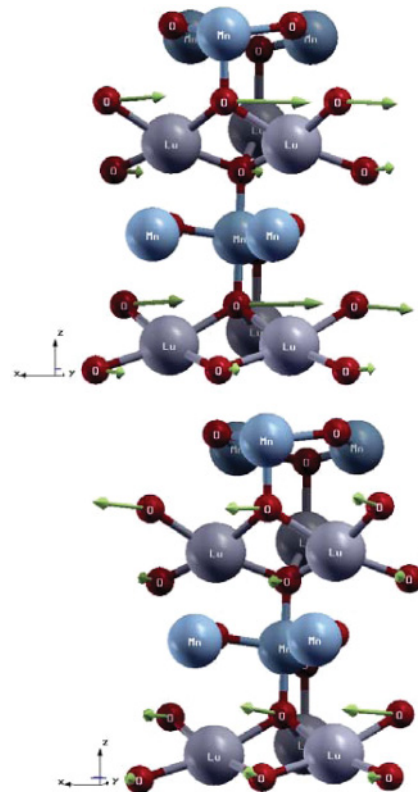


FIG. 6. (Color online) Calculated *E1* symmetry phonon modes for LuMnO<sub>3</sub> near ~320 cm<sup>-1</sup> showing the displacement amplitudes and directions as vector lengths and directions (can be positive or negative), respectively. For these modes with large pressure dependence only the oxygen atoms have significant oscillation amplitudes with O ions moving in the *ab* plane.

The pressure-dependent phonon frequencies are plotted in Fig. 5. Systematically, the phonons harden with the pressure. The phonons in LuMnO<sub>3</sub> and HoMnO<sub>3</sub> are more sensitive to pressure than phonons in YMnO<sub>3</sub>. For the three samples, the phonons with a large hardening rate occur at  $\sim 310$  cm<sup>-1</sup> (labeled E) with 2.74 cm<sup>-1</sup>/GPa (YMnO<sub>3</sub>), 313 cm<sup>-1</sup> (labeled E) with 3.2 cm<sup>-1</sup>/GPa (HoMnO<sub>3</sub>), and 332 cm<sup>-1</sup> (labeled E) with 2.9 cm<sup>-1</sup>/GPa (LuMnO<sub>3</sub>). They are assigned to the *E*<sub>1</sub> mode,<sup>33</sup> which corresponds to the motions of atoms O1, O2, and O3 along a positive direction and atom O4, Mn along a negative direction in the *ab* plane. By calculating the *E*<sub>1</sub> symmetry phonon modes for LuMnO<sub>3</sub> near  $\sim 320$  cm<sup>-1</sup> by the DFT method, we find that these strong pressure-sensitive modes are mainly due to the motion of oxygen atoms. The oxygen atoms have significant oscillatory amplitudes with O ions moving in the *ab* plane under high pressure. Figure 6 displays the calculated displacement amplitudes and directions as vectors on O atoms for *E*<sub>1</sub> ( $\sim 320$  cm<sup>-1</sup>) symmetry phonon modes in ambient pressure LuMnO<sub>3</sub>.

To verify the above results, pressure-dependent near-edge x-ray absorption spectrum measurements on LuMnO<sub>3</sub> were conducted. The Mn *K*-edge near-edge x-ray absorption spectrum of Hex-LuMnO<sub>3</sub> was measured as a function of pressure up to 16 GPa in a diamond anvil pressure cell, which is shown in Fig. 7. No changes in the overall shape of the profile were observed indicating no significant change in the point group up to this pressure. However, an expected shift in the main features is observed (the main “1s to 4p” peak moves up by  $\sim 1.5$  eV with between ambient and 16 GPa pressure). The shift in the peak position can be explained by the “Natoli Rule”<sup>34</sup> given by  $(E_r - E_b)r^2 = \text{constant}$ , where  $E_r$  is the resonance positions (4p or higher *p*-state here) and  $E_b$  is a reference bound state position (pre-edge here). Compression of a coordination shell of radius *r* about Mn will shift the resonance position to higher energies. This is what is observed. The results are consistent with the Mn *K*-edge measurements of Hex-ScMnO<sub>3</sub> (Ref. 8) ( $a = 5.8308$  Å and  $c = 11.1763$  Å) compared to Hex-YMnO<sub>3</sub> (Ref. 8) ( $a = 6.1483$  Å and  $c = 11.4131$  Å) revealing a shift of

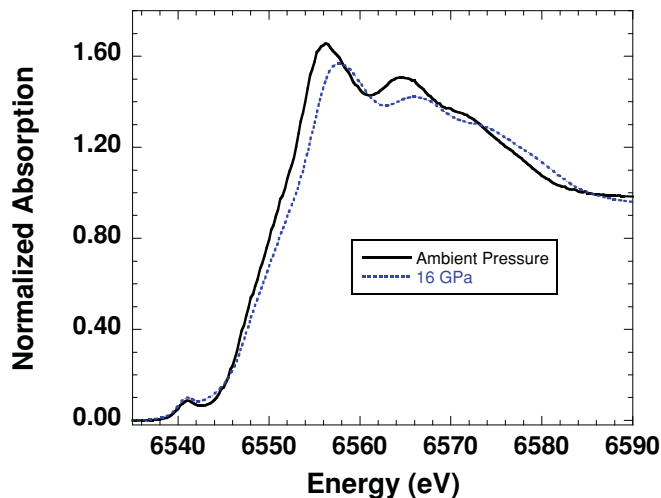


FIG. 7. (Color online) The Mn *K*-edge x-ray absorption spectrum of hexagonal LuMnO<sub>3</sub> at ambient pressure and 16 GPa. Note that the overall shape of the spectra is unchanged. Only a shift of feature positions due to compression is observed.

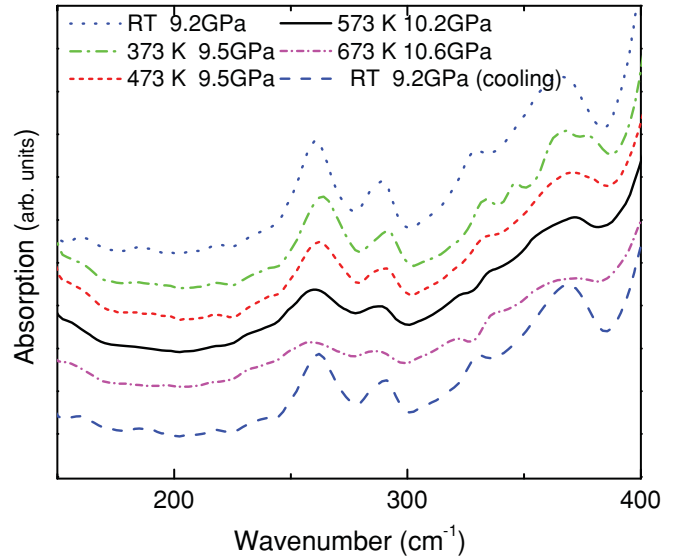


FIG. 8. (Color online) Optical density spectrum of Hex-LuMnO<sub>3</sub> at room temperature (RT): 373, 473, 573, and 673 K with the pressure at  $\sim 10$  GPa for each measurement.

the Sc system to features of higher energy compared to those for the Y system.<sup>35</sup> In both cases, the gross symmetry of the structure is preserved as can be seen in the overall profile shape.<sup>34</sup>

To explore possible temperature dependence, we look at the OD spectra at fixed pressure but varying temperatures. The temperature was kept below 800 K (Ref. 36) to avoid damage to the diamond cell resulting from loss of the adhesive holding the diamond anvils to the seats. The OD spectra in Fig. 8 were taken for temperatures up to 673 K with pressure kept at  $\sim 10$  GPa. No phase change was observed to occur during the heating process. The spectra have the same peak positions and peak profiles after cooling the Hex-LuMnO<sub>3</sub> sample down to room temperature. This again points to the fact that high temperature is the driving mechanism for overcoming the barrier.

The high temperature parent phase (*P6*/*mmc*) has a total dipole moment of zero. For the ferroelectric *P6*<sub>3</sub>*cm* structure, the dipole moment is not zero and is along the *c* axis only. Given the atomic positions, the polarization can be calculated from the unit-cell dipole moment ( $\vec{P} = \sum_i \vec{x}_i Q_i$ ). We used the formal charge values instead of Born effective charges to estimate polarizations. In the Hex-*RMnO*<sub>3</sub>, the Born effective charge is found to be close to the formal charge.<sup>37</sup> The polarizations in Table II were calculated for the ambient pressure structure,

TABLE II. The dipole moment and polarization of Y(Lu)MnO<sub>3</sub> in a *P6*<sub>3</sub>*cm* unit cell (ambient pressure). Results are calculated from crystal structure data in given references.

	Dipole (eÅ)	Polarization ( $\mu\text{C}/\text{cm}^2$ )
YMnO <sub>3</sub>	-2.16	-5.78 (Ref. 43)
	-2.06	-5.51 (Ref. 44)
	-1.75	-4.69 (Ref. 16)
LuMnO <sub>3</sub>	-2.71	-7.55 (Ref. 32)
	-3.89	-10.81 (Ref. 17)

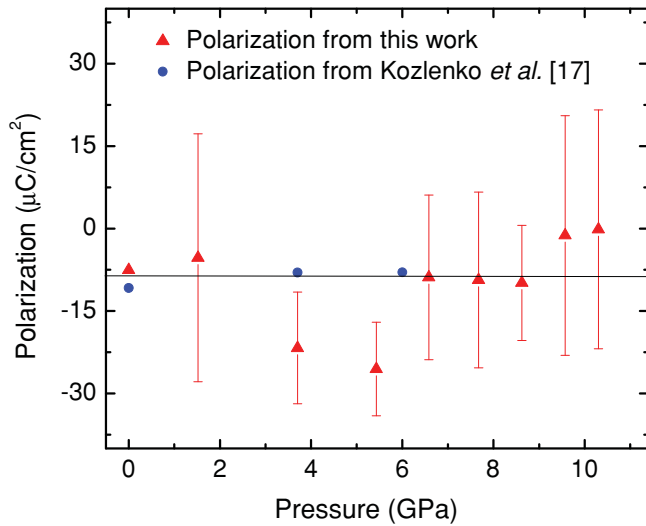


FIG. 9. (Color online) Calculated pressure-dependent spontaneous polarization of Hex-LuMnO<sub>3</sub>.

where the experimental polarization amplitude of Hex-YMnO<sub>3</sub> is 5.5 μC/cm<sup>2</sup>.<sup>38</sup> We plot the pressure-dependent polarization of the Hex-LuMnO<sub>3</sub> sample in Fig. 9, which is estimated from the fit structural parameters. Since the *P*6<sub>3</sub>*cm* structure persists under pressures and the atoms hold their fractional positions, the polarization is approximately constant in the hydrostatic pressure condition.

We now explore changes at higher quasihydrostatic pressures (up to 35 GPa) by the x-ray diffraction method again. The Hex-*RMnO*<sub>3</sub> (002) peak persists in diffraction patterns of LuMnO<sub>3</sub> and YMnO<sub>3</sub> samples at all pressures. At ~23 GPa, the pressure-induced peaks appear in the x-ray diffraction patterns of YMnO<sub>3</sub> and LuMnO<sub>3</sub>, which cannot be indexed by the hexagonal structure. We attribute these peaks to the orthorhombic phase. The x-ray diffraction patterns are from a mixture of hexagonal and orthorhombic phases. At room temperature, only a small amount of the orthorhombic phase is converted and embedded into the Hex-*RMnO*<sub>3</sub> grains for pressures up to ~35 GPa. Normalized high-pressure diffraction patterns of LuMnO<sub>3</sub> and YMnO<sub>3</sub> are plotted in Figs. 10(a) and 10(b). A simulation of the orthorhombic phase is given as the top curve in each figure. For LuMnO<sub>3</sub>, the peaks appear at 2θ = 6.8° and 10.7° at ~22 GPa. With pressure increasing to ~35 GPa, the peak intensities continuously grow. After releasing the pressure, these peaks remain. The pressure-induced peaks are likely the peak (111) at 2θ = 6.76° and the peak (022/211) at 2θ = 11.3° of Ortho-LuMnO<sub>3</sub> at ambient condition. On the sample of YMnO<sub>3</sub>, due to the different chemistry, only one pressure-induced peak appears (2θ = 10.94° at ~24 GPa) and is observed to increase with pressure. It is attributed to the Ortho-YMnO<sub>3</sub> peak (022/211).

Including data points from our measurements and the literature (given below), a qualitative pressure-temperature (P-T) phase diagram of the *RMnO*<sub>3</sub> system (based on the classic YMnO<sub>3</sub>) is plotted in Fig. 11. At ambient pressure, below ~1100 K, the system is in the *P*6<sub>3</sub>*cm* phase.<sup>3</sup> YMnO<sub>3</sub> will start to decompose when the temperature reaches ~1200 K.<sup>39,40</sup> Based on group theory arguments, the aristotype phase is

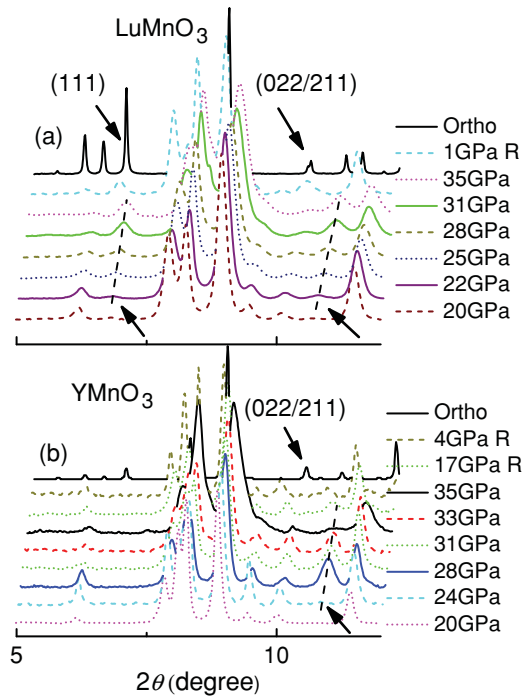


FIG. 10. (Color online) X-ray diffraction patterns at quasihydrostatic pressures. Pressure-induced peaks appear at ~22 (LuMnO<sub>3</sub>) and ~24 GPa (YMnO<sub>3</sub>). The arrow indicates induced peak positions and corresponding peaks in an orthorhombic phase; *R* means pressure release direction of measurement.

predicted to be *P*6<sub>3</sub>/*mcm* at 1105–1360 K (intermediate phase), *P*6<sub>3</sub>/*mmc* at 1360–1600 K, and possibly *P*6/*mmm* above 1600 K.<sup>3</sup> To form Ortho-YMnO<sub>3</sub>, the lowest pressure reported to date was ~3.4 GPa at ~920 K.<sup>41</sup> When the temperature is higher than 1270 K,<sup>6,7,41,42</sup> the required phase transition pressure is reduced significantly. Based on our fixed temperature and fixed pressure experiments, we deduce a mixed phase region of Hex-YMnO<sub>3</sub> and Ortho-YMnO<sub>3</sub>

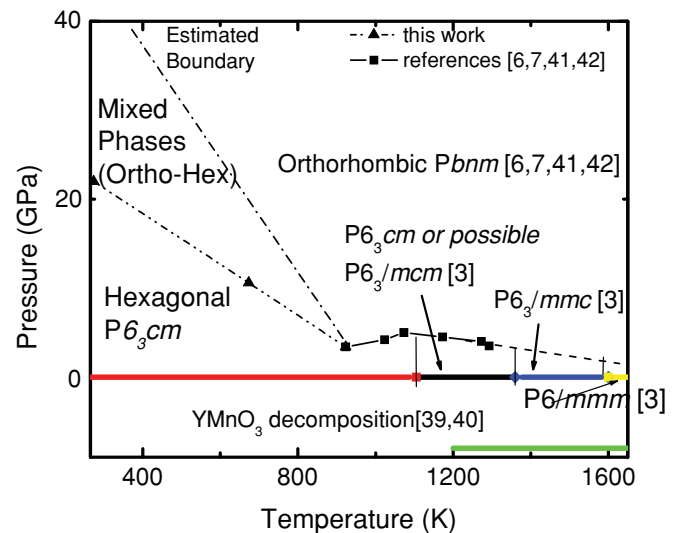


FIG. 11. (Color online) Qualitative pressure-temperature phase diagram for the *RMnO*<sub>3</sub> system (based on the YMnO<sub>3</sub>).

existing for temperatures below 920 K. Apart from the pressure and temperature, another important factor is the time duration for the Ortho-RMnO<sub>3</sub> synthesis, which is not addressed here. Holding the Hex-YMnO<sub>3</sub> at high temperature and high pressure for a long time enhances the transformation.

#### IV. SUMMARY

In conclusion, we have explored the hexagonal RMnO<sub>3</sub> structure under hydrostatic and quasihydrostatic pressures. The hexagonal form of RMnO<sub>3</sub> is a very stable phase for pressures under  $\sim 20$  GPa at ambient temperature as found from x-ray diffraction and x-ray absorption measurements. The unit cell is more readily compressed in the *ab* plane than along the *c* axis. IR measurements reveal that the O atoms are the most sensitive to pressure and have significant oscillation amplitudes with O ions moving in the *ab* plane. A phase transition to a perovskite structure is initiated above  $\sim 22$  GPa. Above  $\sim 22$  GPa, the hexagonal phase starts to be converted into the metastable orthorhombic (perovskite)

phase, but the hexagonal phase is still the majority phase at ambient temperature.

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- <sup>1</sup>K. F. Wang, J.-M. Liu, and Z. F. Ren, *Adv. Phys.* **58**, 321 (2009).  
<sup>2</sup>A. B. Souchkov, J. R. Simpson, M. Quijada, H. Ishibashi, N. Hur, J. S. Ahn, S. W. Cheong, A. J. Millis, and H. D. Drew, *Phys. Rev. Lett.* **91**, 027203 (2003).  
<sup>3</sup>S. Abrahams, *Acta Crystallogr., Sect. B* **65**, 450 (2009).  
<sup>4</sup>O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim, and S. W. Cheong, *Phys. Rev. Lett.* **94**, 087601 (2005).  
<sup>5</sup>D. Fröhlich, S. Leute, V. V. Pavlov, and R. V. Pisarev, *Phys. Rev. Lett.* **81**, 3239 (1998).  
<sup>6</sup>B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, *Phys. Rev. B* **70**, 212412 (2004).  
<sup>7</sup>J. S. Zhou, J. B. Goodenough, J. M. Gallardo-Amores, E. Moran, M. A. Alario-Franco, and R. Caudillo, *Phys. Rev. B* **74**, 014422 (2006).  
<sup>8</sup>K. Uusi-Esko, J. Malm, N. Imamura, H. Yamauchi, and M. Karppinen, *Mater. Chem. Phys.* **112**, 1029 (2008).  
<sup>9</sup>H. Okamoto, N. Imamura, B. C. Hauback, M. Karppinen, H. Yamauchi, and H. Fjellvåg, *Solid State Commun.* **146**, 152 (2008).  
<sup>10</sup>H. W. Brinks, H. Fjellvåg, and A. Kjekshus, *J. Solid State Chem.* **129**, 334 (1997).  
<sup>11</sup>P. A. Salvador, T.-D. Doan, B. Mercey, and B. Raveau, *Chem. Mater.* **10**, 2592 (1998).  
<sup>12</sup>C. Dubourdieu, G. Huot, I. Gelard, H. Roussel, O. I. Lebedev, and G. Van Tendeloo, *Philos. Mag. Lett.* **87**, 203 (2007).  
<sup>13</sup>I. Gelard, C. Dubourdieu, S. Pailhes, S. Petit, and C. Simon, *Appl. Phys. Lett.* **92**, 232506 (2008).  
<sup>14</sup>C. dela Cruz, F. Yen, B. Lorenz, Y. Q. Wang, Y. Y. Sun, M. M. Gospodinov, and C. W. Chu, *Phys. Rev. B* **71**, 060407 (2005).  
<sup>15</sup>M. Janoschek, B. Roessli, L. Keller, S. N. Gvasaliya, K. Conder, and E. Pomjakushina, *J. Phys. Condens. Matter* **17**, L425 (2005).  
<sup>16</sup>D. Kozlenko, S. Kichanov, S. Lee, J. Park, V. Glazkov, and B. Savenko, *JETP Lett.* **82**, 193 (2005).  
<sup>17</sup>D. Kozlenko, S. Kichanov, S. Lee, J. Park, V. Glazkov, and B. Savenko, *JETP Lett.* **83**, 346 (2006).  
<sup>18</sup>D. Kozlenko, S. Kichanov, S. Lee, J. Park, V. Glazkov, and B. Savenko, *Crystallogr. Rep.* **52**, 407 (2007).  
<sup>19</sup>D. P. Kozlenko, I. Mirebeau, J. G. Park, I. N. Goncharenko, S. Lee, J. Park, and B. N. Savenko, *Phys. Rev. B* **78**, 054401 (2008).  
<sup>20</sup>S. M. Feng, L. J. Wang, J. L. Zhu, F. Y. Li, R. C. Yu, C. Q. Jin, X. H. Wang, and L. T. Li, *J. Appl. Phys.* **103**, 026102 (2008).  
<sup>21</sup>A. P. Hammersley, S. O. Svensson, and A. Thompson, *Nucl. Instrum. Methods Phys. Res., A* **346**, 312 (1994).  
<sup>22</sup>R. J. Angel, M. Bujak, J. Zhao, G. D. Gatta, and S. D. Jacobsen, *J. Appl. Crystallogr.* **40**, 26 (2007).  
<sup>23</sup>F. M. Wang and R. Ingalls, *Phys. Rev. B* **57**, 5647 (1998).  
<sup>24</sup>W. A. Bassett and E. Huang, *Science* **238**, 780 (1987).  
<sup>25</sup>T. A. Tyson, T. Wu, K. H. Ahn, S. B. Kim, and S. W. Cheong, *Phys. Rev. B* **81**, 054101 (2010).  
<sup>26</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).  
<sup>27</sup>B. Toby, *J. Appl. Crystallogr.* **34**, 210 (2001).  
<sup>28</sup>I. Loa, P. Adler, A. Grzechnik, K. Syassen, U. Schwarz, M. Hanfland, G. K. Rozenberg, P. Gorodetsky, and M. P. Pasternak, *Phys. Rev. Lett.* **87**, 125501 (2001).  
<sup>29</sup>A. A. Bossak, I. E. Graboy, O. Y. Gorbenko, A. R. Kaul, M. S. Kartavtseva, V. L. Svetchnikov, and H. W. Zandbergen, *Chem. Mater.* **16**, 1751 (2004).  
<sup>30</sup>S. Geller, J. B. Jeffries, and P. J. Curlander, *Acta Crystallogr., Sect. B* **31**, 2770 (1975).  
<sup>31</sup>S. Lee, A. Pirogov, M. Kang, K.-H. Jang, M. Yonemura, T. Kamiyama, S. W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda, and J. G. Park, *Nature (London)* **451**, 805 (2008).  
<sup>32</sup>B. B. Van Aken, A. Meetsma, and T. T. M. Palstra, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **57**, i101 (2001).



- <sup>33</sup>M. N. Iliev, H. G. Lee, V. N. Popov, M. V. Abrashev, A. Hamed, R. L. Meng, and C. W. Chu, *Phys. Rev. B* **56**, 2488 (1997).
- <sup>34</sup>C. R. Natoli, edited by K. O. Hodgson, B. Hedman and J. E. Penner-Hahn, *EXAFS and Near Edge Structure III* (Springer-Verlag, New York, 1984), p. 38.
- <sup>35</sup>C. T. Wu, Y. Y. Hsu, B. N. Lin, and H. C. Ku, *Physica B* **329-333**, 709 (2003).
- <sup>36</sup>A. Jayaraman, *Rev. Mod. Phys.* **55**, 65 (1983).
- <sup>37</sup>T. Tohei, H. Moriwake, H. Murata, A. Kuwabara, R. Hashimoto, T. Yamamoto, and I. Tanaka, *Phys. Rev. B* **79**, 144125 (2009).
- <sup>38</sup>N. Fujimura, T. Ishida, T. Yoshimura, and T. Ito, *Appl. Phys. Lett.* **69**, 1011 (1996).
- <sup>39</sup>I. K. Jeong, N. Hur, and T. Proffen, *J. Appl. Crystallogr.* **40**, 730 (2007).
- <sup>40</sup>M. Chen, B. Hallstedt, and L. J. Gauckler, *J. Alloys Compd.* **393**, 114 (2005).
- <sup>41</sup>B. B. Van Aken, Ph.D. dissertation, University of Groningen, 2001.
- <sup>42</sup>V. E. Wood, A. E. Austin, E. W. Collings, and K. C. Brog, *J. Phys. Chem. Solids* **34**, 859 (1973).
- <sup>43</sup>G. Nénert, M. Pollet, S. Marinel, G. R. Blake, A. Meetsma, and T. T. M. Palstra, *J. Phys. Condens. Matter* **19**, 466212 (2007).
- <sup>44</sup>B. B. Van Aken, A. Meelsma, and T. T. M. Palstra, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **57**, 230 (2001).