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Article

Pressure-Induced Transformation of 6H Hexagonal to 3C Perovskite Structure in $PbMnO_3$

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A tetragonal perovskite $PbMnO_3$ was obtained by treating the 6H hexagonal perovskite phase at 15 GPa and 1273 K. Structural analysis using synchrotron X-ray diffraction suggested that $PbMnO_3$ crystallizes in the centrosymmetric space group *P*4/*mmm*, unlike $PbTiO_3$ and $PbVO_3$ which have a polar structure in space group *P*4*mm*. Iodometric titration revealed the presence of the oxygen deficiency of $x = 0.06$ for $PbMnO_{3-x}$. The hexagonal 6H and the 3C perovskite phases exhibited antiferromagnetic ordering at 155 and 20 K, respectively.

Introduction

Lead-transition metal perovskites attract attention as candidate magnetic ferroelectric materials in which ferroelectricity and magnetism coexist. The stereochemical effect of the $6s^2$ lone pair of Pb^{2+} ions and the covalent Pb−O bond are expected to stabilize distorted acentric structures, as in $PbTiO_3$, the only lead-3*d* transition metal perovskite obtained at ambient pressure.[1] Other magnetic lead-transition metal perovskites such as $PbVO_3$,[2−4] $PbCrO_3$,[5,6] and $PbFeO_3$[7] can be stabilized by high-pressure (HP) synthesis. $PbVO_3$ is isostructural with $PbTiO_3$, but its tetragonal distortion, $c/a = 1.229$, is much larger than that of $PbTiO_3$ ($c/a = 1.064$). We found that $PbVO_3$ has a two-dimensional magnetism attributable to d_{xy} orbital ordering and proposed that this orbital ordering in the d^1 system was one of the reasons for the large tetragonal distortion.[4] $PbCrO_3$ with Cr^{4+} (d^2) ions is a cubic perovskite.[5] The deficiencies of Pb and O ions with a long periodicity were recently found.[6] $PbFeO_3$ with an orthorhombic unit cell of $6a \times 2a \times 2a$ (where a is the lattice constant of a cubic perovskite) has been prepared recently, but its crystal structure has not yet been determined.[7] The structures of lead-transition metal perovskites differ depending on the transition metal ions, and we have focused our attention on $PbMnO_3$ with Mn^{4+}(d^3) ions.

The only previously reported $PbMnO_3$ synthesized at HP had a hexagonal perovskite-type structure,[8] but hexagonal perovskites are known to exhibit sequential structural changes due to the application of pressure. The stacking of the closely packed oxygen layers in the hexagonal perovskites changed from *ab* (2H) to *ababcbcac* (9R), *abac* (4H), *abcacb* (6H), and finally to *abc* (3C) as the synthesis pressure was

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increased.[9] $BaMnO_3$, for example, changed from the 2H to the 9R structure at 7.5 GPa and from the 9R to the 4H structure at 9 GPa. $SrMnO_3$, on the other hand, changed from the 4H to the 6H structure at 5 GPa. The hexagonal 6H fluorides $CsMnF_3$, $RbNiF_3$, and $TlNiF_3$ changed to a 3C perovskite structure at 3 GPa.[9] We therefore tried to convert $PbMnO_3$ from a hexagonal perovskite structure to a 3C-type perovskite structure by applying pressures up to 15 GPa. We found that $PbMnO_3$ prepared at 8 GPa and 1073 K had the 6H-type hexagonal perovskite structure and that it could be transformed to the 3C-type perovskite structure by treating it at 15 GPa and 1273 K. We also investigated the structures and the magnetic properties of the 6H and 3C $PbMnO_3$ obtained this way.

Experimental Section

The hexagonal perovskite phase of $PbMnO_3$ was prepared from a stoichiometric mixture (equal parts PbO, PbO_2, and Mn_2O_3). The mixture was sealed in a gold capsule and treated for 30 min at 1073 K and 8 GPa in a cubic-anvil-type HP apparatus. The obtained hexagonal $PbMnO_3$ was sealed in a gold capsule and treated for 30 min at 1273 K and 15 GPa in a Kawai-type double-stage HP apparatus. Tungsten carbide anvils with a truncated edge length of 8 mm were used, and the pressure medium was a semisintered MgO octahedron. A $LaCrO_3$ sleeve was placed in the center of the pressure medium as a thermal insulator. The sample capsule sealed with an insulating BN sleeve was inserted into the $LaCrO_3$ sleeve with a Pt heater. $LaCrO_3$ plugs were stuffed into both ends of the heater, and both ends of the heater were folded for the electrodes.

The synchrotron X-ray powder diffraction (SXRD) patterns for both hexagonal perovskite and 3C perovskite $PbMnO_3$ samples were collected with a large Debye−Scherrer camera installed at the BL02B2 beam line of SPring-8,[10] and the XRD results were analyzed using the Rietveld method with the RIETAN-2000 program.[11] The oxygen content of the samples was determined by an iodometric titration with an automatic titration meter (TOA DKK, AUT-301), and magnetic properties were measured with a SQUID magnetometer (Quantum Design, Model MPMS XL). The temperature dependence of the magnetic susceptibility was measured in a magnetic field of 1000 Oe upon heating after cooling in a zero field (ZFC) and then on cooling (FC). The magnetization data were collected at 5 K in magnetic fields from −50 to +50 kOe.

Results and Discussion

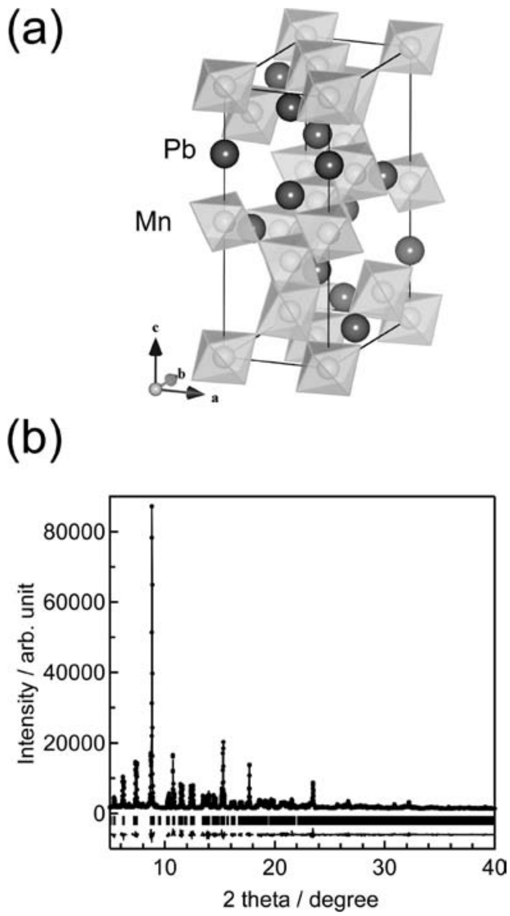

Figure 1. (a) Crystal structure of 6H $PbMnO_3$ with a monoclinic unit cell. (b) Observed (dots), calculated (line), and difference (lower line) of the SXRD pattern of 6H $PbMnO_3$ at room temperature ($\lambda = 0.42199$ Å). The tick marks correspond to the positions of Bragg reflections.

Table 1. Refined Crystallographic Parameters for 6H $PbMnO_3$ ($Z = 12$)[a]

atom	site	g	x	y	z	B (Å^2)
Pb1	4e	1	0	−0.0022(5)	0.25	1.01(5)
Pb2	8f	1	−0.0016(5)	0.3331(4)	0.0872(2)	1.21(5)
Mn1	4a	1	0	0	0	0.25(7)
Mn2	8f	1	0.0039(11)	0.3282(14)	0.8433(5)	0.25
O1	4e	1	0	0.536(8)	0.25	1.0
O2	8f	1	0.271(11)	0.239(6)	0.254(5)	1.0
O3	8f	1	−0.020(15)	0.834(7)	0.078(5)	1.0
O4	8f	1	0.244(13)	0.081(8)	0.081(4)	1.0
O5	8f	1	0.734(13)	0.082(8)	0.074(5)	1.0

[a] Space group $C2/c$ (no. 15), $a = 5.4896(1)$ Å, $b = 9.5147(6)$ Å,$c = 13.5442(9)$ Å, $\beta = 88.896(2)°$, $V = 707.30(8)$ Å^3, $R_{WP} = 6.05\%$, $R_I = 3.34\%$. The isotropic atomic displacement parameters B for oxygen atoms were fixed to 1.0 Å^2.

Figure 1 shows the SXRD pattern for $PbMnO_3$ synthesized at 8 GPa. The data in the ranges without the difference plot were excluded in the refinement because of the presence of reflections from unidentified impurities. The Rietveld analysis of the SXRD data revealed that the $PbMnO_3$ synthesized at 8 GPa was isostructural with $Ba_3LuIr_2O_9$, which has a monoclinically distorted 6H hexagonal perovskite structure in space group $C2/c$.[12] The structural parameters are summarized in Table 1. The iodometric titration showed that the 6H structure had almost no oxygen deficiency. The oxygen content was 2.99(1).

Since $PbMnO_3$ synthesized at 8 GPa had a 6H hexagonal structure, treating it at a higher pressure was expected to transform it into a 3C-type perovskite. Figure 2 shows the SXRD pattern of $PbMnO_3$ treated at 15 GPa and 1273 K. As expected, a 3C perovskite was produced. No extra peak due to the presence of a super structure was found. As shown in the inset, the 100 and 001 peaks split, indicating the tetragonal distortion. The SXRD peaks were indexed with a unit cell of $a = 3.8562$ Å and $c = 3.9209$ Å. The density of

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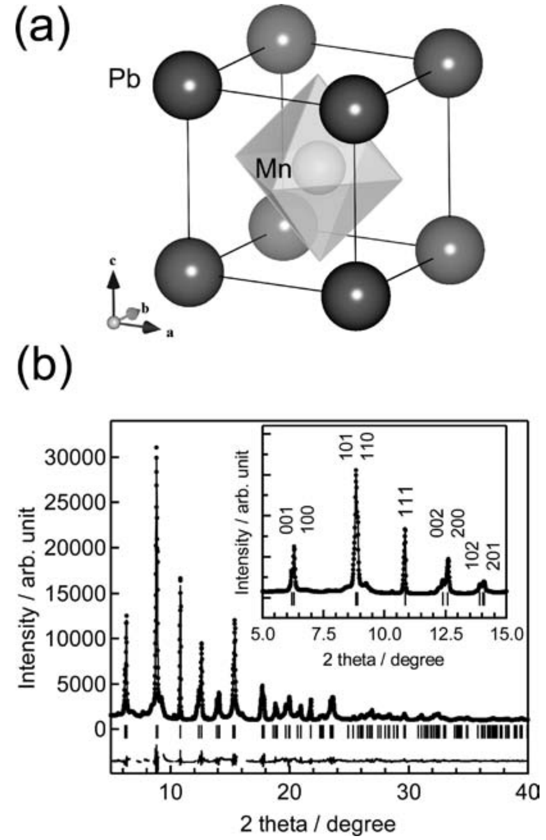

Figure 2. (a) The crystal structure of 3C $PbMnO_3$. (b) Observed (dots), calculated (line), and difference (lower line) of the SXRD pattern of 3C $PbMnO_3$ at room temperature ($\lambda = 0.42261$ Å). The tick marks correspond to the positions of Bragg reflections. Inset is the magnified view of the SXRD pattern between 5° and 15°.

the 6H $PbMnO_3$ was 8.74 g cm^{-3}, and that of the 3C $PbMnO_3$ was 8.83 g cm^{-3}.

Although the perovskite $PbMnO_3$ had a tetragonal structure with a c/a ratio of 1.017, it was not electrically polarized. The structural refinement was first attempted assuming a $PbTiO_3$-type structure in space group $P4mm$, but the atomic coordinates converged at values close to those for a centrosymmetric structure. The z coordinates were 0.50(1) for Mn1, 0.07(1) for O1, and 0.54(1) for O2. The final R_{WP} parameter for the $P4mm$ model was 6.76%, almost the same as the R_{WP} parameter for the centrosymmetric model with a $P4/mmm$ space group (6.78%). These almost negligible atomic displacements in the $P4mm$ model and the fact that the lowering of the symmetry from $P4/mmm$ to $P4mm$ does not improve the fitting result strongly suggest that the actual symmetry is $P4/mmm$. The tetragonal distortion is not a polar one. The final structural parameters for the $P4/mmm$ model are summarized in Table 2.

The iodometric titration revealed that the valence of Mn in the 3C perovskite phase was 3.88(1)+. This indicates that the perovskite $PbMnO_3$ was oxygen-deficient, probably because of the imperfect sealing during the heat treatment at 15 GPa, and was actually $PbMnO_{2.94(1)}$.

The temperature dependence of the magnetic susceptibility and the magnetization curves of 6H and 3C $PbMnO_3$ are plotted in Figures 3 and 4. The 6H $PbMnO_3$ showed a magnetic transition at a Néel temperature (T_N) of 155 K

Table 2. Refined Crystallographic Parameters for 3C $PbMnO_3$ ($Z = 1$)[a]

atom	site	g	x	y	z	B (Å^2)
Pb1	1a	1	0	0	0	0.59(2)
Mn1	1d	1	0.5	0.5	0.5	0.05(5)
O1	1c	0.98	0.5	0.5	0	0.77(15)
O2	2e	0.98	0.5	0	0.5	0.77

[a] Space group $P4/mmm$ (no. 123), $a = 3.8561(3)$ Å, $c = 3.9209(4)$ Å, $V = 58.300(8)$ Å^3, $R_{WP} = 6.78\%$, $R_I = 2.18\%$. The occupation factors of oxygen atoms were fixed to be $PbMnO_{2.94}$.

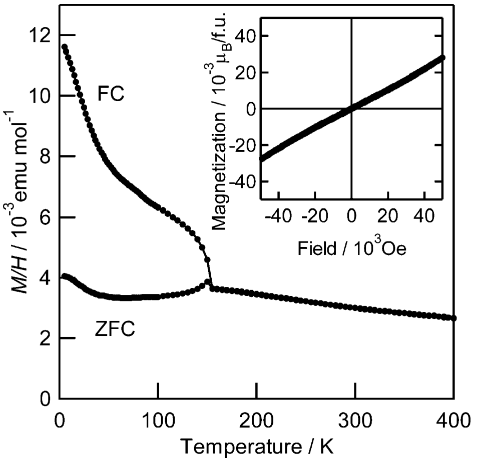

Figure 3. Temperature dependence of the magnetic susceptibility of 6H $PbMnO_3$ measured under 1000 Oe. Inset is the magnetization curve measured at 5 K.

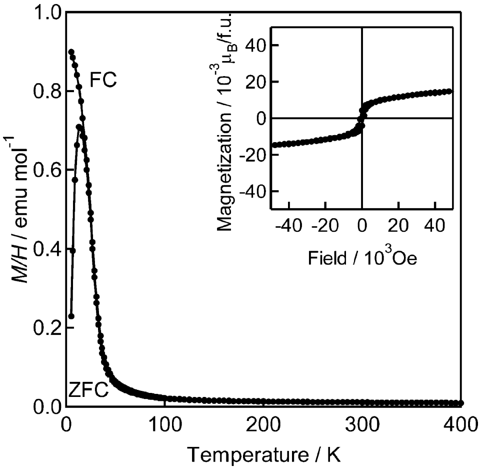

Figure 4. Temperature dependence of the magnetic susceptibility of 3C $PbMnO_3$ measured under 1000 Oe. Inset is the magnetization curve measured at 5 K.

(Figure 3). Fitting the susceptibility data between 200 and 400 K to the Curie−Weiss equation $\chi = C/(T - \theta) + \chi_0$ (where C is the Curie constant, θ is the Weiss temperature, and χ_0 is the temperature-independent term) gives $C = 1.87(22)$ emu·K/mol, $\theta = -400(40)$ K, and $\chi_0 = 0.3(2) \times 10^{-3}$ emu/mol. This Curie constant differs insignificantly from the $C = 1.88$ emu·K/mol expected for a Mn^{4+} ($S = 3/2$) localized spin system with a gyrometric ratio of 2.0. This result is also consistent with the absence of an oxygen deficiency. The magnetic behavior of 6H $PbMnO_3$ is similar to that of another 6H hexagonal perovskite with Mn^{4+}, $SrMnO_3$. $SrMnO_3$ prepared at 6.5 GPa had a Weiss temperature of −280 K, showed a magnetic transition at 90 K, and showed parasitic ferromagnetic behavior below that temperature.[13] The T_N/θ ratios for 6H $PbMnO_3$ and 6H $SrMnO_3$ were almost identical. The FC and the ZFC data for 6H $PbMnO_3$ did not coincide below 160 K, suggesting that the sample is weakly ferromagnetic because of spin canting. The magnetization curve at 5 K shown in the inset of Figure 3 was, however, far from simple. The data collected under increasing and decreasing fields did not differ. Furthermore, the slope was steeper below −30 kOe and above +30 kOe. We currently have no explanation for these peculiar behaviors.

The 3C $PbMnO_3$ showed a magnetic transition at 20 K (Figure 4). Since the Weiss temperature is negative, as discussed later, this compound is basically an antiferromagnet. The observed T_N is considerably lower than the T_N values reported for other 3C-type perovskites with Mn^{4+}: $SrMnO_3$ (233 K)[14] and $CaMnO_3$ (130 K).[15] This can be explained by the presence of Mn^{3+} as a consequence of oxygen deficiency. According to the Kanamori−Goodenough rules, ferromagnetic coupling is expected between ions with filled and empty e_g orbitals. Mn^{3+} has a $t_{2g}{}^3e_g{}^1$ electronic configuration, and Mn^{4+} has a $t_{2g}{}^3$ electronic configuration. Ferromagnetic coupling between Mn^{3+} and Mn^{4+} disturbs the Mn^{4+} antiferromagnetic network and therefore reduces T_N. The magnetization curve showed ferromagnetic behavior with hysteresis. Since the Mn ion occupies the site with an inversion symmetry in the *P*4/*mmm* model, this ferromagnetic-like behavior cannot be attributed to the spin canting. It might be due to the formation of ferromagnetic clusters. The fitting to the Curie−Weiss equation in the temperature range of 200 to 400 K gives $C = 2.38(4)$ emu·K/mol, $\theta = -68(2)$ K, and $\chi_0 = 0.455(6) \times 10^{-4}$ emu/mol. The estimated Curie constant of 3C $PbMnO_3$ is larger than that of 6H $PbMnO_3$. This difference in Curie constants can be explained by the presence of Mn^{3+} ions with $S = 2$ as a consequence of the oxygen deficiency.

Conclusion

An oxygen-deficient 3C perovskite phase of $PbMnO_3$ was prepared by treating the monoclinic 6H hexagonal phase at 15 GPa and at 1273 K. Although the 3C phase had a tetragonal distortion with a *c*/*a* ratio of 1.017, the crystal structure was not polar like the crystal structures of $PbTiO_3$ and $PbVO_3$. Both phases exhibited magnetic ordering: the 6H phase, at 155, and the 3C phase, at 20 K.

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