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Realization of Intrinsic Colossal Magnetoresistance in $Pb(Pb_{1/3}Hg_{2/3})_3Mn_4O_{12}$: An A Site-Ordered Quadruple Perovskite Oxide

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However, A-site-ordered AA'₃B₄O₁₂-type quadruple perovskite oxides exhibit significantly suppressed double exchange due to their extremely small B–O–B bond angles (\approx 140°), hindering the realization of intrinsic CMR effects. Here, we report the design and synthesis of a novel quadruple perovskite oxide Pb-(Pb_{1/3}Hg_{2/3})₃Mn₄O₁₂ (PPHMO) characterized by an unusually increased Mn–O–Mn bond angle of up to 153°. This compound crystallizes into a cubic Im $\overline{3}$ structure with the charge distribution



 $Pb^{2+}(Pb_{1/3}^{3.5+}Hg_{2/3}^{2+})_{3}Mn_{4}^{3.63+}O_{12}$. A ferromagnetic phase transition is observed at the Curie temperature $T_{C} \approx 120$ K, accompanied by an insulator-to-metal transition. Furthermore, applying magnetic fields significantly reduces the resistivity, resulting in intrinsic CMR effects with an absolute MR value of 650% at 8 T, increasing to 2250% at 16 T near T_{C} . The large intrinsic MR is thereby realized unprecedentedly in an A-site-ordered quadruple perovskite oxide. Related origins for the intrinsic CMR effects presented in the current PPHMO are discussed in detail.

INTRODUCTION

The colossal magnetoresistance (CMR) effect,¹⁻⁷ characterized by a substantial change in resistivity across several orders of magnitude under the influence of a magnetic field, has garnered significant attention in solid state chemistry, condensed matter physics and materials science. This interest stems from the profound interactions among spin, charge, and orbital degrees of freedom, as well as its promising applications in magnetic storage devices and advanced sensors.⁸⁻¹¹ The intrinsic CMR effect, where the maximum MR occurs near the ferromagnetic Curie temperature $T_{\rm C}$, is particularly prominent in doped perovskite manganites with the general formula $RE_{1-x}AE_xMnO_3$ (RE = trivalent rare earth; AE = divalent alkaline earth). The substitution of divalent or trivalent ions introduces holes or electrons, resulting in the coexistence of Mn³⁺ and Mn⁴⁺ magnetic ions. According to the doubleexchange (DE) theory,^{12–14} the itinerant e_g electrons that hop between Mn^{3+} and Mn^{4+} ions are strongly coupled with localized t_{2g} electrons via Hund's coupling, leading to ferromagnetic ordering. Consequently, the para-to-ferromagnetic phase transition observed in manganites within specific doping ranges is often accompanied by an insulator-to-metal

transition. Applying a magnetic field near $T_{\rm C}$ suppresses spin fluctuations, facilitating the hopping of e_g-state carriers and significantly reducing resistivity. Thus, the DE mechanism is a critical condition for realizing the CMR effects in manganites.

Compared with simple ABO₃-type perovskites, intrinsic CMR effects have not yet been observed in A-site-ordered quadruple perovskite oxides with the chemical formula $AA'_{3}B_{4}O_{12}$. In this ordered structure, the A' site is typically occupied by 3d transition metal ions exhibiting strong Jahn–Teller effects, such as Mn^{3+} and Cu^{2+} , forming square-planar $A'O_4$ units.^{15–17} Since both A' and B sites can host magnetic transition metals, quadruple perovskites exhibit a broad range of intriguing physical properties, including intermetallic charge transfer,¹⁸ charge disproportionation,¹⁹ magnetoelectric multiferroicity,^{20–22} high-performance half-metallicity,²³ and cata-

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Figure 1. (a) SXRD and refined patterns of PPHMO at RT with the space group $Im\overline{3}$. Observed (red dots), calculated (black line), difference (green line), background (blue line), and possible peak positions (pink ticks) are displayed. Inset shows a local magnified view. (b) Crystal structure of PPHMO. The B-site MnO₆ octahedra and A'-site Pb/HgO₄ squares connect with each other by sharing corner O. SAED patterns along the, (c) [001], (d) [110], and (e) [111] zone axes, respectively. The diffraction spots are indexed according to the space group $Im\overline{3}$. The red circles show the spots that cannot been indexed with a prototype simple cubic structure.

lyst activity.²⁴ However, due to the smaller ionic size of the A' site, the BO_6 octahedra undergo severe tilting, reducing the B-O-B bond angle to approximately 140° in AA'₃B₄O₁₂ quadruple perovskites. This significant distortion hinders the hopping of eg electrons at the B site, such as that observed in quadruple-perovskite-type manganites, suppressing the DE mechanism and the resultant CMR effects. Thus, achieving substantial intrinsic MR effects remains an open challenge in A-site-ordered quadruple perovskite oxides. In principle, stabilizing larger A'-site ions to reduce BO₆ octahedral titling is key to enhance MR effects. Beyond smaller ions such as Is key to enhance for energy beyond smaller ions such as Mn^{3+} and Cu^{2+} , larger ions such as Hg^{2+} and Pb^{4+} can also occupy the A' site and alleviate BO_6 tilting in quadruple perovskites, as demonstrated in $Pb^{2+}Hg_3^{2+}Ti_4^{4+}O_{12}^{25}$ and $PbCoO_3$ (i.e., $Pb^{2+}Pb_3^{4+}Co_2^{2+}Co_2^{3+}O_{12}$ with 1:3 ordered Pb^{2+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{2+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and Pb^{4+} at the A site and 1:1 endergy Cc_2^{3+} and Cc_2^{3+} and CcPb²⁺ and Pb⁴⁺ at the A site, and 1:1 ordered Co²⁺ and Co³⁺ at the B site).²⁶ Building on this concept, we designed and synthesized a new quadruple perovskite manganite with the chemical and charge formation as $Pb^{2+}(Pb_{1/3}^{3.5+}Hg_{2/3}^{2+})_3Mn_4^{3.63+}O_{12}$ using high-pressure and high-temperature conditions. The introduction of larger Pb^{3.5+} (on average) and Hg²⁺ randomly distributed at the A' site, significantly increases the B-O-B bond angle to 153°, favoring DE interactions between mixed Mn³⁺ and Mn⁴⁺ at the B site. Consequently, large intrinsic MR effects have been realized in an A-site-ordered quadruple perovskite oxide for the first time.

EXPERIMENTAL SECTION

Polycrystalline Pb(Pb_{1/3}Hg_{2/3})₃Mn₄O₁₂ (PPHMO) was synthesized via a solid-state reaction using a Walker-type two-stage high-pressure apparatus. High-purity (\geq 99.9%) HgO, PbO, and MnO₂ powders were used as starting materials, mixed in a stoichiometric ratio of 1:1:2 and ground thoroughly in an agate mortar to ensure homogeneity. The resulting mixture was compacted and sealed into

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a gold capsule. Due to the toxicity of HgO and PbO, all procedures were conducted in an argon-filled glovebox to ensure safety. The sealed capsule was then treated under conditions of 18 GPa and 1473 K for 30 min. After the heating process, the heating system was deactivated, and the pressure was gradually released to ambient conditions.

To determine the phase composition and analyze the crystallographic structure, powder synchrotron X-ray diffraction (SXRD) was performed at a wavelength of 0.4201 Å on beamline BL02B2 at SPring-8 in Japan at room temperature (RT). Selected area electron diffraction (SAED) was performed at RT using a JEOL ARM200F transmission electron microscope equipped with double Cs correctors (CEOS) for the condenser and objective lens along the [001], [110], and [111] zone axes, respectively. Structural parameters were refined through Rietveld analysis using GSAS software.^{27,28} For valence state identification, high-resolution Pb-L₃ X-ray absorption spectroscopy (XAS) spectra were measured using the partial fluorescence yield method at the Taiwan inelastic X-ray scattering BL12XU beamline at SPring-8 at RT. Mn- $L_{2,3}$ XAS measurements were conducted at beamline TLS11A at the National Synchrotron Radiation Research Center in Taiwan using the total electron yield mode at RT. Magnetic susceptibility and magnetization were measured using a superconducting quantum interference device magnetometer (MPMS-VSM, Quantum Design). Resistivity and MR measurements were performed using a physical property measurement system (PPMS, Quantum Design).

RESULTS AND DISCUSSION

Figure 1a shows the SXRD pattern of PPHMO collected at RT. The prominent diffraction peaks can be indexed with a simple cubic perovskite structure with a lattice parameter $a_p = 3.823$ Å. However, a few faint diffraction peaks, such as those observed at 10.0 and 11.8°, cannot be explained by this simple cubic model, suggesting the presence of superstructural diffraction. To investigate these structural characteristics further, high-resolution SAED was performed. As illustrated in Figure 1c, additional diffraction spots (highlighted with red

circles) appear along the [001] zone axis, confirming the occurrence of superlattice diffraction in the prototype cubic structure. Similar superlattice spots were also observed in the SAED patterns along the [110] and [111] zone axes, as shown in Figure 1c,e, respectively. By expanding the unit cell to $a = 2a_p$ in a cubic framework, all electron diffraction, as well as the faint diffraction peaks in SXRD pattern, can be successfully indexed. Therefore, the current PPHMO structure is best described using a cubic $2a_p \times 2a_p \times 2a_p$ superstructural model.

Based on the SAED analysis, the diffraction conditions of PPHMO can be summarized as hkl (h + k + l = 2n), 0kl (k + l = 2n), hhl (l = 2n), and h00 (h = 2n). These conditions are consistent with several cubic space groups, including $Im\overline{3}$ (No. 204), I23 (No. 197), I432 (No. 211), $I\overline{4}3m$ (No. 217), and $Im\overline{3}m$ (No. 229). Each space group was temporarily used to refine the SXRD pattern. By comparison, the $Im\overline{3}$ space group provided the best goodness of fit (Figure 1a) and yielded reliable structural parameters, which are summarized in Table 1. Consequently, the most probable space group of PPHMO is assigned to $Im\overline{3}$, consistent with prior reports for PbHg₃Ti₄O₁₂.²⁵

Table 1. Structure Parameters of PPHMO with the Space Group $Im\overline{3}$ Refined from the SXRD Pattern at RT^{a}

atom	site	x	у	z	G	$U_{\rm iso} (\times 100 { m \AA}^2)$
Pb1	2a	0	0	0	1.0	1.87(4)
Pb2	6b	0	0.5	0.5	0.33	1.04(2)
Hg	6b	0	0.5	0.5	0.67	1.04(2)
Mn	8c	0.25	0.25	0.25	1.0	0.31(4)
0	24g	0	0.2897(8)	0.2050(10)	1.0	0.42(5)
bond length			value (Å)	bond angle		value (deg)
Pb1-O (×12)			2.714(9)	∠Pb1–O–Mn		88.6(3)
Pb2/Hg-O (×4)			2.245(4)	∠Pb2/Hg−O−Mn		103.4(2)
Mn-O (×6)			1.966(1)	∠Mn-O-Mn		153.0(2)
^a Crysta occupa	al data: ncy. R _v	space § _{vp} = 7.3	group $Im\overline{3}$ (N 7%, $R_{\rm p} = 5.4$	lo. 204), <i>a</i> = 7 8%.	7.64562	(3) Å. G: site

In the $Im\overline{3}$ symmetry of PPHMO, the A-site 2a (0, 0, 0) Wyckoff position is occupied by Pb, while the A'-site 6b (0, (0.5, 0.5) position is randomly occupied by Pb and Hg in a 1:2 ratio. The B-site 8c (0.25, 0.25, 0.25) accommodates Mn, and oxygen atoms are located at the 24g (0, y, z) position, forming an AA'₃B₄O₁₂-type quadruple perovskite structure. The crystal structure is illustrated in Figure 1b. Compared to the simple perovskite structure of ABO₃, PPHMO forms a 1:3 ordered structure at the A site. This ordered arrangement will reduce the translational symmetry. As a result, the lattice constant is doubled and related superlattice diffraction peaks appear. The refined structural parameters are summarized in Table 1. The Pb at the A site in PPHMO exhibits a Pb-O bond length of 2.714 Å, similar to the value observed in $PbHg_3Ti_4O_{12}$ (2.728 Å),²⁵ suggesting the presence of Pb^{2+} at this site. At the A' site, the Pb/Hg-O bond length in the square-planar Pb/HgO4 units is 2.245 Å, which is significantly larger than the A'-Olengths observed in isostructural Mn-based compounds $CaCu_3Mn_4O_{12}$ (1.941 Å)¹⁷ and LaCu₃Mn₄O₁₂ (1.965 Å),² where transition metals occupy the A' site and Mn occupies the B site. This sharply increased A'-O bond length in PPHMO results in a significant increase in the Mn-O-Mn bond angle at the B site, from 141° in Ca/LaCu₃Mn₄O₁₂ to 153° in the present compound. This increased bond angle

plays a crucial role in enabling the large intrinsic MR effects (shown later). In addition, the B-site Mn–O bond length of PPHMO (1.966 Å) is located at the intermediate between the Mn^{3+} –O (2.020 Å in LaMnO₃)³⁰ and Mn^{4+} –O length (1.903 Å in SrMnO₃),³¹ implying the occurrence of mixed Mn³⁺ and Mn⁴⁺ charge states in PPHMO, consistent with the XAS results presented below.

Figure 2a shows the high-resolution XAS patterns at the Pb- L_3 edge, alongside those of PbTiO₃ (Pb²⁺ reference) and



Figure 2. (a) Pb- L_3 XAS of PPHMO together with PbNiO₃ as a Pb⁴⁺ reference and PbTiO₃ as a Pb²⁺ reference. The inset shows the spectral integral area of I_{6s} after subtracting the background. (b) XAS of Mn- $L_{2,3}$ for PPHMO together with those of BiMn₃Cr₄O₁₂ with Mn³⁺ at the square-planar A' site, LaMnO₃ with Mn³⁺ and HgMnO₃ with Mn⁴⁺ in octahedral coordination environment at the B site. The orange triangle curve stands for the superposition of HgMnO₃ and LaMnO₃ with a ratio of 0.63:0.37.

PbNiO₃ (Pb⁴⁺ reference) for comparison.^{32,33} In PbNiO₃, a distinct absorption peak I_{6s} is observed at the pre-edge, corresponding to the dipole allowed excitation of an electron from the $2p_{3/2}$ core level to the unoccupied 6s states, a characteristic feature of the Pb⁴⁺ valence state.³⁴ Conversely, this transition is prohibited in PbTiO₃ due to the fully occupied 6s states for Pb²⁺. For PPHMO, the presence of a pre-edge peak indicates the existence of Pb⁴⁺. To evaluate the Pb4+ content, the broad background was modeled using a combination of an arctan-like function and Gaussian functions, representing the edge jump and 6d electron states, respectively.³⁵ As shown in the inset of Figure 2a, the I_{6s} integral area of PPHMO is approximately 38% of that observed in PbNiO₃. This result allows us to estimate the average valence state of Pb in PPHMO to be approximately +2.75. Since the A site is occupied all by Pb²⁺ considering the bond length and coordination environment, one-third of A' site will

have approximately 25% Pb^{2+} and 75% Pb^{4+} (i.e., $Pb^{3.5+}$ on average). Given the stable charge state of Hg^{2+} , the average valence state of Mn at the B site is estimated to be +3.63 (+3.625 to be precise) based on charge conservation.

XAS at the $L_{2,3}$ edges is known to be highly sensitive to the valence states^{36,37} and local environments^{38,39} of 3*d* transition metals. For an open d shell, an increase in valence by one typically results in a 1-2 eV shift of the white line in the X-ray absorption spectrum toward higher photon energies, along with significant changes in the spectral line shape. To further confirm the valence state of Mn in PPHMO, XAS spectra of Mn- $L_{2,3}$ were measured. As shown in Figure 2b, the white line of PPHMO can be well reproduced by a superposition of the spectra for HgMn⁴⁺O₃⁴⁰ and LaMn³⁺O₃, which share the same coordination environment for Mn ions as PPHMO, at a ratio of 0.63:0.37. This result indicates the formation of an average $Mn^{3.63+}$ valence state at the B site, consistent with the Pb-L₃ edge findings. Additionally, the Mn- $L_{2,3}$ spectrum of PPHMO lacks features related to BiMn₃Cr₄O₁₂²¹ where Mn³⁺ exhibits a square-planar coordination environment, confirming the absence of Mn at the A' site in PPHMO. Therefore, the charge configuration of PPHMO can be assigned as $Pb^{2+}(Pb_{1/3}^{3.5+}Hg_{2/3}^{2+})_{3}Mn_{4}^{3.63+}O_{12}.$

Figure 3a presents the temperature dependence of the magnetic susceptibility of PPHMO, measured under a 0.1 T



Figure 3. (a) Temperature dependence of magnetic susceptibility and inverse susceptibility measured at 0.1 T for PPHMO. The T_C is determined by a tangential method as shown by the green lines. The pink line indicates the Curie–Weiss fitting. (b) Field dependence of magnetization at selected temperatures.

field in both zero-field-cooling (ZFC) and field-cooling (FC) modes. As the temperature decreases, the susceptibility sharply increases around $T_{\rm C} \approx 120$ K, indicating the occurrence of a ferromagnetic-like phase transition. This behavior can be understood based on the magnetic interaction between the mixed Mn³⁺ and Mn⁴⁺ ions at the B site via the DE mechanism. Above 160 K, the inverse susceptibility follows the

Cuire–Weiss law, expressed as $\chi^{-1} = (T - \theta)/C$, where the Weiss temperature is fitted as $\theta = 121.9$ K and the Curie constant $C = 18.25 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1} \cdot \text{Oe}^{-1}$. The positive value of θ confirms the ferromagnetic interaction and its proximity to $T_{\rm C}$ is consistent with the transition temperature. From the Curie constant, the effective magnetic moment is calculated as μ_{eff} = 12.08 $\mu_{\rm B}$ /f.u., which exceeds the theoretical value of 8.56 $\mu_{\rm B}$ / f.u., assuming the spin-only moment of Mn ions with the configuration charge o f Pb- $(Pb_{1/3}Hg_{2/3})_3(Mn_{0.63}^{4+}Mn_{0.37}^{3+})_4O_{12}$. This discrepancy is likely due to the formation of ferromagnetic clusters, as reported in other perovskite manganites.^{41,42} Below $T_{\rm S} \approx 31$ K, the ZFC and FC curves separate from each other, and the ZFC curve decreases further upon cooling. This phenomenon likely results from the presence of short-range spin clusters in the ferromagnetic background. It can be attributed to the disorder of A'-site ions, which induces a local random potential and consequently leads to local competition between the ferromagnetic state driven by DE interactions and antiferromagnetic state driven by superexchange interactions. Similar phenomena have also been observed in other doped manganites.^{41,43-45} Figure 3b depicts the field dependence of magnetization for PPHMO. Above T_{C} , a linear magnetization behavior is observed, consistent with the paramagnetic state. Below $T_{\rm C}$, such as at 2 K, the material exhibits a canonical soft ferromagnetic hysteresis loop, with a magnetization up to 10.0 $\mu_{\rm B}$ /f.u. at 7 T and a coercive field of approximately 250 Oe.

Since the DE driving ferromagnetic phase transition occurs in PPHMO, a corresponding electrical variation is expected near T_C. To investigate this, electrical transport properties of PPHMO were measured under different magnetic fields and temperatures. Figure 4a shows the resistivity as a function of temperature at fixed fields. At zero field, the resistivity increases continuously with decreasing temperature above $T_{\rm C}$, indicating insulating electrical behavior. However, as the temperature approaches $T_{\rm C}$, the resistivity undergoes a sharp drop, signaling an insulator-to-metal transition. Upon further cooling to 34 K, an upturn in resistivity is observed, and this temperature is very close to T_s, where the ZFC and FC magnetic susceptibility curves begin to separate from each other. This suggests that the scattering mechanism responsible for the resistivity increase is likely spin-dependent and may originate from the Kondo-like effects.⁴⁵ When an 8 T magnetic field is applied, the resistivity decreases significantly, particularly near $T_{\rm C}$, and the metallization transition shifts to a higher temperature. Moreover, the resistivity further reduces under a higher field of 16 T. It can be clearly observed that the maximum MR value appears near $T_{\rm C}$ in the temperature-dependent MR curves, as shown in the inset of Figure 4a, revealing the occurrence of an intrinsic CMR effect in PPHMO.⁴⁶ Here, the values of MR are calculated as MR(%) = $[(\rho(H) - \rho(0 T))]/\rho(H) \times 100\%$.

Field-scanning resistivity measurements at fixed temperatures further enabled the calculation of MR values that vary with the magnetic field. As shown in Figure 4b, the MR effect at 300 K (in the paramagnetic state) is negligible. However, at temperatures slightly below $T_{\rm C}$ (e.g., at 100 K), a pronounced negative CMR effect is observed, with an absolute value of 650% at 8 T and increasing to 2250% at 16 T. This is the first observation of intrinsic CMR effects in quadruple perovskite oxides to date, and it is comparable with those observed in canonical CMR materials such as simple ABO₃ perovskite manganites La_{1-x}Sr_xMnO₃ (MR \approx 1200% at 15 T near $T_{\rm C}$ for x = 0.175).⁴⁷ At temperatures far below $T_{\rm C}$ (e.g., at 2 K), the



Figure 4. (a) Temperature dependence of resistivity measured at different magnetic fields for PPHMO. The inset shows the temperature-dependent MR curves at different fields. (b) Field dependence of MR effect at three selected temperatures. The inset displays the low-field MR behavior.

MR effect diminishes compared to that near $T_{\rm C}$. Notably, PPHMO exhibits a significant low-field MR effect at lower temperatures. For instance, at 2 K, applying a 0.5 T field induces an absolute MR value of up to 40% as shown in the inset of Figure 4b. This high low-field MR value is desirable for practical applications, such as magnetic sensing. The low-field MR effect resembles that reported in other Mn-based isostructural compounds, such as Ca/La/BiCu₃Mn₄O₁₂,^{48–50} where MR behavior is extrinsic and attributed to interdomain or grain tunneling of spin-polarized electrons at temperatures well below $T_{\rm C}$. However, unlike these analogues, PPHMO demonstrates large intrinsic MR effects near $T_{\rm C}$, which distinguishes it from other Mn based isostructural compounds.

Next, the possible origins of the intrinsic CMR effects observed in PPHMO are discussed. As mentioned previously, even in the isostructural $La/BiCu_3Mn_4O_{12}^{49,50}$ that contain mixed Mn³⁺ and Mn⁴⁺ at the B site, no intrinsic MR is observed near T_C. Other A-site doped quadruple perovskite manganite oxides, such as La/Na_{1-x}Ca_xMn₃Mn₄ \hat{O}_{12}^{51} and Hg_{1-x}Na_xMn₃Mn₄ O_{12}^{52} also do not show intrinsic MR effect. A key structural difference lies in the B-site Mn-O-Mn bond angle, which is approximately 140° in the aforementioned materials but increases to 153° in PPHMO. This corresponds to a significant decrease in the B-site distortion angle θ_d (= $180^{\circ} - \angle Mn - O - Mn$). As a result, the bandwidth (W) of the B-site Mn will increase according to the first-order approximation $W \propto (\cos \theta_{\rm d})/d^{3.5}$, where d represents the average B-O bond length (d should be almost constant if the valence state of B-site Mn is fixed).⁵³ The minimal Mn-O-Mn bond angle strongly limits the DE interaction between Mn^{3+} and Mn^{4+} ions via the linking O^{2+} ions in the abovementioned materials; hence, intrinsic MR effects are suppressed in these compounds. In contrast, benefiting from the larger A'-site ionic size, the B-site Mn-O-Mn bond angle of PPHMO sharply increases (i.e., the distortion angle sharply decreases) and is close to those observed in doped simple perovskite manganites such as the La_{1-x}Ca_xMnO₃ CMR family $(\approx 160^{\circ})$.⁵⁴ This will enhance the bandwidth of Mn. In other words, the magnetic interaction between Mn³⁺ and Mn⁴⁺ in PPHMO primarily depends on the electron hopping along the Mn³⁺-O-Mn⁴⁺ pathways. The Mn-e_g and O-2p orbitals have a large overlap as the Mn-O-Mn bond angle is close to 180°, which is favorable for electron hopping and results in PPHMO undergoing a ferromagnetic phase transition accompanied by a metallization transition. Applying an external magnetic field will significantly increase the probability of electron hopping near $T_{\rm C}$ leading to the realization of intrinsic CMR effects in a quadruple perovskite oxide for the first time.

In addition to the DE mechanism, electronic phase separation and random potential effects induced by dopingrelated quenched disorder also contribute to the CMR effects, as reported in doped manganites.^{3,5,55,56} In PPHMO, the disordered distribution of Pb/Hg at the A' site can also lead to random potential effects and phase fluctuations, further influencing the emergence of CMR. Further theoretical studies are necessary to establish the detailed mechanisms underlying the CMR effects in PPHMO.

CONCLUSIONS

In this study, a new quadruple perovskite oxide, PPHMO was designed and synthesized under high-pressure and hightemperature conditions. The compound crystallizes in the cubic $Im\overline{3}$ space group with a lattice parameter a = 7.64562(3)Å. Based on XAS measurements, the charge configuration was determined to be $Pb^{2+}(Pb_{1/3}^{3.5+}Hg_{2/3}^{2+})_{3}Mn_{4}^{3.63+}O_{12}$. At $T_{C} \approx$ 120 K, the compound undergoes a para-to-ferromagnetism transition concurrently with an insulator-to-metal transition. Remarkably, the application of a magnetic field significantly reduces resistivity, resulting in negative intrinsic CMR effects. The absolute MR value reaches 650% at 8 T and increases further to 2250% at 16 T near $T_{\rm C}$, representing the record-high MR value observed in quadruple perovskite oxides to date. Additionally, PPHMO exhibits a notable low-field MR of approximately 40% at 0.5 T and 2 K. The observed CMR effects are primarily attributed to the activation of the DE interaction, enabled by the unusually increased Mn-O-Mn bond angle. These findings establish PPHMO as a prototype material for studying large intrinsic MR properties in A-siteordered quadruple perovskite oxides.

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Notes

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ABBREVIATIONS

CMR, colossal magnetoresistance; DE, double-exchange; PPHMO, Pb(Pb_{1/3}Hg_{2/3})₃Mn₄O₁₂; FC, field-cooling; RT, room temperature; SAED, selected area electron diffraction; SXRD, synchrotron X-ray diffraction; XAS, X-ray absorption spectroscopy; ZFC, zero-field-cooling

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