A-site Randomness Effect on Structural and Physical Properties of Ba-based Perovskite Manganites

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The discovery of novel structural and physical properties in the A-site ordered manganite RBA₆O₉ (R = Y and rare earth elements) has demanded new comprehension about perovskite manganese oxides. In the present study, the A-site disordered form, R₀.₅Ba₀.₅MnO₃, has been investigated and compared with both RBA₆O₉ and R₀.₅A₀.₅MnO₃ (A: Sr, Ca) in the structures and electromagnetic properties. R₀.₅Ba₀.₅MnO₃ has a primitive cubic perovskite cell in the structure and magnetic glassy states are dominant as its ground state, in contrast to the ordinary disordered R₀.₅A₀.₅MnO₃ (A: Sr, Ca). In Pr-compounds with various degrees of Pr/Ba randomness at the A-sites, the A-site disorder gradually suppresses both ferromagnetic and A-type antiferromagnetic transitions and finally leads to a magnetic glassy state in Pr₀.₅Ba₀.₅MnO₃. A peculiar behavior, multi-step magnetization and resistivity change, has been observed in Pr₀.₅Ba₀.₅MnO₃. These properties could be closely related to any spatial heterogeneity caused by the random distribution of Ba²⁺ and R³⁺ with much different ionic radius.

KEYWORDS: A-site ordered/disordered perovskite manganites, Crystal structure, Electromagnetic properties, Randomness effect, Magnetoresistance effect

§1. Introduction

The magnetic and electrical properties of perovskite manganites with the general formula (R₁₋ₓAₓ⁺)₃MnO₃ (R = rare earth elements and A = Ca and Sr) have been extensively investigated for the last decade. Among the interesting features are the so-called colossal magnetoresistance (CMR) and metal-insulator (MI) transition accompanied by charge/orbital order (CO). It is now widely accepted that these enchanting phenomena are caused by the strong correlation/competition among spin, charge and orbital degrees of freedom, which would be significantly influenced by the A-site randomness. Recently we successfully synthesized the A-site ordered manganite, RBA₆O₉ (R = Y and rare earth elements) and reported its structure and electromagnetic properties.⁴⁻⁶ As schematically shown in Fig. 1, the most significant structural feature of RBA₆O₉ is that the MnO₂ square sublattice is sandwiched by two types of rock-salt layers, RO and BaO, with much different sizes, and consequently the MnO₆ octahedron itself is distorted in a noncentrosymmetric manner that both Mn and oxygen atoms in the MnO₂ plane are displaced toward the RO layer (Fig. 1(c)), in contrast to the rigid MnO₆ octahedron in the A-site disordered manganite (R₁₋ₓAₓ⁺)₃MnO₃ (A = Ca and Sr). This means that the structural and physical properties of RBA₆O₉ can be no longer explained in terms of the basic structural distortion, the so-called tolerance factor $f$, as can be in ($R₀.₅A₀.₅$)MnO₃ (A = Ca and Sr). Fig. 2 shows the electronic phase diagram of RBA₆O₉ expressed as a function of the ratio of ionic radius of the A-site cations. Among possible combinations of R/Ba, the mismatch between RO and BaO is the smallest in La/Ba and the largest in Y/Ba. As seen in Fig. 2, the CE-type charge/orbital ordered state (COI(CE)) with a new stacking variation of the CE-type CO is stabilized at the relatively high temperatures ($T_{CO}$) far above 300 K, when $R³⁺$ is smaller than Sm³⁺ in ion size. The high $T_{CO}$ would be not only due to the absence of A-site randomness but also due to the distorted structure with a tilt of MnO₆ octahedra as well as heavy distortion of MnO₆ octahedra.⁵ The new CE-type CO with a 4-fold periodicity along the c-axis (4CE-CO) could be due to a layer type order of $R$ and Ba.⁴ Interestingly, this 4CE-CO changes into a new type with a two or single periodicity along the c-axis, when the system enters into the antiferromagnetic CE-type charge/orbital ordered state (AFI(CE)).⁵ Furthermore, RBA₆O₉ ($R$ = Tb, Dy, Ho and Y) shows the structural transition at $T₁$ above $T_{CO}$, as shown in Fig. 2, which is possibly accompanied by a $d_{x²−y²}$ type orbital order.⁴ Therefore the degeneracy of orbital, charge and spin degrees of freedom are lifted in these compounds. On the other hand, RBA₆O₉ ($R$ = La, Pr and Nd) with relatively larger $R³⁺$ has no octahedral tilt and shows a transition from a paramagnetic metal (PM) to a ferromagnetic metal (FM). The ground states for PrBa₆O₉ andNdBa₆O₉ are the A-type antiferromagnetic metal (AFM(A)). In LaBa₆O₉, AFI(CE)
manganese oxides. Recently, theoretical studies also have revealed that the interesting properties such as CMR and electronic phase separation come from a critical competition between FM and an antiferromagnetic CO interaction, which could be significantly influenced by the A-site randomness or a fluctuation of the local structure. The A-site disordered form \((R_{0.5}Ba_{0.5})MnO_3\) with the same constituent elements is crucial to deepen the understanding of the structural and physical properties of perovskite manganites; it may make clear the effects of A-site randomness not only qualitatively but also quantitatively. Very recently Akahoshi et al. reported that the magnetic glassy state became dominant in \((R_{0.5}Ba_{0.5})MnO_3\). However, the detailed structure and electromagnetic properties of \((R_{0.5}Ba_{0.5})MnO_3\) has not been reported. We have also independently synthesized the A-site disordered Ba-based manganite \((R_{0.5}Ba_{0.5})MnO_3\) and studied the structure and electromagnetic properties in terms of the degree of A-site randomness. In this paper, we report the structures and electromagnetic properties of \((R_{0.5}Ba_{0.5})MnO_3\), especially Pr-compounds with various degrees of the randomness of Pr/Ba at the A-sites, and we will discuss the obtained results in terms of the A-site randomness effect.

§2. Experimental

Polycrystalline samples of \((R_{0.5}Ba_{0.5})MnO_3\) \((R = Y \text{ and rare earth elements})\) were prepared by a solid-state reaction of \(R_2O_3\), BaCO\(_3\) and MnO\(_2\) at 1623 K in 1% \(O_2/Ar\) gas for 1 day, followed by annealing at 1173 K in \(O_2\) gas for 1 day (Path I in Fig. 3). The preparation method of the ordered form \(RBA\text{Mn}_2O_6\) was reported elsewhere. Interestingly, annealing \(RBA\text{Mn}_2O_6\) under \(O_2\) gas at high temperatures always resulted in insufficient \(R/Ba\) solid-solution at the A-sites. Pr-compounds: \([\text{Pr}_{0.5}Ba_{1-g}]\text{Pr}_{1-g})Ba_2Mn_2O_6\] \((0.5 \leq g \leq 1.0)\) with various degrees of the A-site order were synthesized from \(PrBa\text{Mn}_2O_6\) by controlling the annealing time and temperatures \((1273 \sim 1623 \text{ K})\) in \(O_2\) gas (Path II in Fig. 3), where \([ \text{Pr}\] or \([ \text{B}]\) represents Pr-sites (or Ba-sites) in \(PrBa\text{Mn}_2O_6\). The degree of A-site order \((S)\), \(S = (2g-1) \times 100 \%\), was determined by the Rietveld analysis of powder X-ray and neutron diffractions. We obtained \(S = 96 \pm 2\%\) for the ordered form \(PrBa\text{Mn}_2O_6\) and \(S = 0.0 \%\) for the disordered form \(Pr_{0.5}Ba_{0.5}MnO_3\) prepared by Path I in Fig. 3. In the present study, we successfully prepared Pr-compounds: \([\text{Pr}_{0.5}Ba_{1-g}]\text{Pr}_{1-g})Ba_2Mn_2O_6\] \((0.5 \leq g \leq 1.0)\) with \(S = 96(2)\%\), 87(4)\%, 70(4)\%, 57(6)\%, 32(2)\%, 25(6)\% and 0.0\% which were named as PB96, PB87, PB70, PB57, PB32, PB25 and PB00, respectively. The synthesis conditions of these Pr-compounds are shown in Table I.

The crystal structures including the order/disorder of \(R/Ba\) were refined by the Rietveld analysis of powder X-ray and neutron diffractions using RIETAN 2000. The magnetic ordered states at low temperatures were studied by powder neutron diffraction. The X-ray powder diffraction experiments were performed using a MXP21...
Table 1. Synthesis conditions of Pr-compounds (PB96~PB00) with various degrees of the A-site randomness. (See the text).

| Sample   | Synthesis condition                                                                 |
|----------|-------------------------------------------------------------------------------------|
| PB96     | Heating starting materials at 1623 K in pure Ar for 24 h, followed by annealing at 623 K in O₂ for 24 h |
| PB87     | Annealing PB96 at 1273 K in O₂ for 6 h                                               |
| PB70     | Annealing PB87 at 1523 K in O₂ for 24 h                                              |
| PB57     | Annealing PB70 at 1523 K in O₂ for 24 h                                               |
| PB32     | Annealing PB57 at 1623 K in O₂ for 24 h                                               |
| PB25     | Annealing PB32 at 1623 K in O₂ for 24 h                                               |
| PB00     | Heating starting materials at 1623 K in 1% O₂/Ar for 24 h, followed by annealing at 1173 K in O₂ for 24 h |

Fig. 3. Flowchart of sample preparation.

Mac Science diffractometer with the following operation conditions: 5˚ < 2θ < 120˚ with the step size of 0.02˚, Cu-Kα radiation, V = 45 kV and I = 350 mA. The powder neutron diffraction was performed with the Kiken powder diffractometer, HERMES, of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. Neutrons with a wavelength of 1.8207 Å were obtained by the 331 reflection of the Ge monochromator and the 12'-blank-sample-22' collimation. The magnetic properties were studied using a SQUID magnetometer in a temperature range T = 2~400 K. The electric resistivity of a sintered pellet was measured for T = 2~400 K by a conventional four-probe technique.

§3. Results and discussion

3.1 The A-site disordered R₀.₅Ba₀.₅MnO₃

The X-ray diffraction patterns of all R₀.₅Ba₀.₅MnO₃ can be indexed in the primitive cubic perovskite cell. There is no extra peak suggesting a superstructure. The lattice parameters of R₀.₅Ba₀.₅MnO₃ at room temperature are shown in Fig. 4. The lattice parameter decreases with decreasing ionic radius of R₃⁺. The simple cubic mean no tilt of MnO₆ octahedra in contrast to the orthorhombic GdFeO₃ type distortion of R₀.₅A₀.₅MnO₃ (A = Ca and Sr). In general, the mismatch between the larger MnO₂ and the smaller (RₐA)O sublattices is relaxed by tilting MnO₆ octahedra, resulting in the lattice distortion from cubic to, mostly, the orthorhombic GdFeO₃-type structure. In this distortion, the bond angle ∠Mn-O-Mn deviates from 180˚, leading to a significant change in the effective one-electron bandwidth or equivalent e_g-electron transfer interaction, and the degree of this mismatch is described as f = ⟨(rₐ) + r₀) / √2[ (rₐMn + r₀) ] , where ⟨rₐ⟩, rₐMn and r₀ are (averaged) ionic radii for the respective elements. The electronic phase diagram of R₀.₅A₀.₅MnO₃ (A = Ca and Sr) has been explained by f; FM state generated by the double-exchange interaction is dominant near f = 1, while COI(CE) state is most stabilized in the lower f region (f < 0.975). In R₀.₅Ba₀.₅MnO₃, the f is in the range from 1.026 (La/Ba) to 0.995 (Y/Ba), which are rather close to f = 1, comparing to the variation 0.955 < f < 1 in R₀.₅A₀.₅MnO₃ (A = Ca and Sr). Therefore the simple cubic structures of R₀.₅Ba₀.₅MnO₃ can be partly understood from the f-values close to 1, that is relatively small mismatch between MnO₂ and (R₀.₅Ba₀.₅)O lattices. Here, it should be noticed that the f is greater than 1 in R₀.₅Ba₀.₅MnO₃ (R = La, Pr and Nd). Actually the lattice parameters (3.904 ~ 3.918 Å) of these compounds are larger than the ideal one (∼3.89 Å) of Mn₃⁺O₂ lattice. From simple cubic structures of R₀.₅Ba₀.₅MnO₃, one may expect FM generated by double exchange interaction as the stable electronic state. The ground state of La₀.₅Ba₀.₅MnO₃ is actually a pure FM and the ferromagnetic transition temperature T_C decreases by 50 K compared with T_C = 330 K in LaBaMn₂O₆, agreeing with the previous report. On the other hand, Pr₀.₅Ba₀.₅MnO₃ and Nd₀.₅Ba₀.₅MnO₃ show the increase of magnetic susceptibility (M/H) below about 150 K and then show glassy behaviors below about 50 K, evidenced by significant differences of M/H-T curves on zero-field cooled (ZFC) and field cooled (FC) processes. As an example, the M/H-T curve for Nd₀.₅Ba₀.₅MnO₃ is shown in Fig. 5(a), to-
gether with that for NdBaMn$_2$O$_6$. Akahoshi et al.$^{11}$ previously reported FM states for Pr$_{0.5}$Ba$_{0.5}$MnO$_3$ and Nd$_{0.5}$Ba$_{0.5}$MnO$_3$, which could be due to imperfect disorder as verified in the following section of this paper. More typical spin-glass behaviors have been observed in $R_{0.5}$Ba$_{0.5}$MnO$_3$ with Sm$^{3+}$ and smaller R$^{3+}$s, agreeing with the previous report$^{11}$. The typical $M/H$-$T$ curves of Sm$_{0.5}$Ba$_{0.5}$MnO$_3$ and Y$_{0.5}$Ba$_{0.5}$MnO$_3$ are shown in Fig. 5(b) and 5(c) together with those for SmBaMn$_2$O$_6$ and YBaMn$_2$O$_6$. YBaMn$_2$O$_6$ particularly shows three successive transitions; the structural transition at $T_s$, CO transition at $T_{CO}$ and antiferromagnetic transition at $T_N$. The magnetic interaction is ferromagnetic above $T_C$, while below $T_C$ it is antiferromagnetic.$^{2,3,5}$ In Y$_{0.5}$Ba$_{0.5}$MnO$_3$, on the other hand, there is no evidence or no trace of the transitions observed in YBaMn$_2$O$_6$, except for the spin-glass (SG) transition at $T_G = 30$ K. The electrical resistivities of $R_{0.5}$Ba$_{0.5}$MnO$_3$ ($R = \text{Nd, Sm and Y}$) show semiconducting behaviors, as shown in Fig. 6. The activation energy $E_a$ decreases with decreasing the ionic radius of $R^{3+}$ ion.

The results of magnetic properties of $R_{0.5}$Ba$_{0.5}$MnO$_3$ are summarized in Fig. 4 as the phase diagram. Here we compare the phase diagram among $R$BaMn$_2$O$_6$, $R_{0.5}$Ba$_{0.5}$MnO$_3$ and $R_{0.5}$A$_{0.5}$MnO$_3$ ($A = \text{Ca and Sr}$). The electronic states characteristic of perovskite manganites such as AFM(CE) and COI(CE) seen in RBaMn$_2$O$_6$ and $R_{0.5}$A$_{0.5}$MnO$_3$ ($A = \text{Ca and Sr}$) are absent in $R_{0.5}$Ba$_{0.5}$MnO$_3$. Instead of these states, magnetic glassy states govern the electronic state of $R_{0.5}$Ba$_{0.5}$MnO$_3$. The magnetic glassy state could be due to a disorder effect that hinders magnetic long-range ordering and it could occur as a result of the competition between randomly distributed ferromagnetic and antiferromagnetic interactions. Since the ionic radius of Ba$^{2+}$ ($= 1.61$ Å)$^{15}$ is much larger than that of Sr$^{2+}$ ($= 1.44$ Å)$^{15}$ and R$^{3+}$ ($\leq 1.36$ Å)$^{15}$. $R_{0.5}$Ba$_{0.5}$MnO$_3$ could include any spatial heterogeneity in a nanometer scale, which results in magnetic nonhomogeneous states.

Fig. 4. Lattice parameters at room temperature and phase diagram of the A-site disordered $R_{0.5}$Ba$_{0.5}$MnO$_3$ as a function of the tolerance factor $f$. SG: spin glass phase.

Fig. 5. Temperature dependence of magnetic susceptibility for the A-site ordered/disordered (a) NdBaMn$_2$O$_6$/Nd$_{0.5}$Ba$_{0.5}$MnO$_3$, (b) SmBaMn$_2$O$_6$/Sm$_{0.5}$Ba$_{0.5}$MnO$_3$ and (c) YBaMn$_2$O$_6$/Y$_{0.5}$Ba$_{0.5}$MnO$_3$ under 0.1 T.

Fig. 6. Temperature dependence of resistivity for the sintered $R_{0.5}$Ba$_{0.5}$MnO$_3$ ($R = \text{Nd, Sm and Y}$) sample.
Only the largest La$^{3+}$ among $R^{3+}$s forms a homogeneous solid-solution at the $A$-sites with Ba$^{2+}$ and the magnetic long-range ordering of FM is realized in La$_{0.5}$Ba$_{0.5}$MnO$_3$.

It has been suggested that the electromagnetic properties of perovskite manganites with $A$-site cations randomly distributed depend on not only $f$ but also the variance of $A$-cation radius distribution $\sigma^2$ defined as $\sigma^2 = \frac{1}{n} \sum_i y_i r_i^2 - r_A^2$, where $r_i$ is the ionic radius of each $A$-site cation, $y_i$ is the fractional occupancy of the $i$ ion, $r_A$ is the average ionic radius of $A$-site cations.$^{16}$ The value of $\sigma^2$ indicates the magnitude of potential disorder effect. Here, we discuss the ground states of the $A$-site disordered systems $R_{0.5}A_{0.5}$MnO$_3$ ($A =$ Ca, Sr and Ba) in terms of $\sigma^2$. Figure 7 shows the mapping of $R_{0.5}A_{0.5}$MnO$_3$ ($A =$ Ca, Sr and Ba) on a $\sigma^2$ vs. $\langle r_A \rangle$ diagram. The data of $R_{0.5}A_{0.5}$MnO$_3$ ($A =$ Sr and Ca) are quoted from the previous literatures.$^{1,17}$ The thick lines in Fig. 7 represent possible phase boundaries. The magnetic long-range orderings (AFI, AFM and FM) tend to be stabilized in the lower $\sigma^2$ region ($\sigma^2 < 10^{-2}$); otherwise, the magnetic glassy state is obviously dominant above $\sigma^2 = 10^{-2}$, except FM in La$_{0.5}$Ba$_{0.5}$MnO$_3$. Thus the difference of the ionic radius between $A$-site cations significantly influences magnetic long-range ordering in perovskite manganites. In connection with the disordered effect, the lowering of both $T_C$ and $T_{C\text{O}}$ in the critical region is not recognized in the phase diagram of RBaMn$_2$O$_6$ in contrast to $R_{0.5}A_{0.5}$MnO$_3$ ($A =$ Sr and Ca). The absence of such critical behavior in RBaMn$_2$O$_6$ is partly due to the $A$-site ordering. In the critical region where FM (AFM) and CO interactions compete against each other, they are significantly affected by fluctuation of composition, coherent size of crystal and external field etc, that is the $A$-site randomness, and such fluctuation of interactions enhances the criticality. On the other hand, it could be more definite in the $A$-site ordered RBaMn$_2$O$_6$ which interaction becomes dominant or which electronic state is stable.

3.2 The $A$-site randomness effect in Pr-compounds

As mentioned above, the structure and electromagnetic properties of perovskite manganites are significantly affected by the $A$-site disorder. In this section, we report the relation between those and the degree of the $A$-site disorder in Pr-compounds (PB96 $\sim$ PB00) with various degrees of the $A$-site randomness. Figure 8 shows X-ray diffraction patterns of the $A$-site ordered PrBaMn$_2$O$_6$ (PB96) and disordered Pr$_{0.5}$Ba$_{0.5}$MnO$_3$ (PB00). The inset shows (00$\bar{2}$)$_p$ reflections of Pr-compounds (PB96 $\sim$ PB00) with various degrees of Pr/Ba randomness at the $A$-sites.
dependent $M/H$ below $T_N$. On the other hand, PB32 and PB25 with a considerable $A$-site disorder exhibit clear FM transitions at $T_C = 158$ K and 152 K, respectively. Since the saturated values of $M/H$ of PB32 and PB25 are lower than that expected from full moment, any short-range magnetic ordered phase and/or AFM(A) phase coexist with FM phase. The rather low $T_C$s for the second group (PB32 and PB25) compared with $T_C$s for the first group (PB96-PB70) suggests two types of FM phase in Pr-compounds. This might be reflected in the $M/H - T$ curve with two peaks around 200 K and 180 K for the intermediate compound PB57, namely PB57 includes two FM phases and each FM phase transforms to AFM(A) phase at independent temperatures (200 K and 180 K), showing peaks in $M/H-T$ curve. Finally, the perfect disordered PB00 has a much smaller $M/H$ than that of other compounds and shows a spin glass like transition at 50 K, as shown in the inset of Fig. 10(a). A small amount of AFM(A) phase was confirmed at low temperature by a neutron diffraction measurements, but FM long-range ordered phase was not observed.

The obtained results of Pr-compounds are summarized in Fig. 10(b). The $A$-site order stabilizes AFM(A) state associated with a $d_{x^2-y^2}$ orbital order (layer type), because the layer type order of $R/Ba$ and consequently the distorted MnO$_6$ octahedra introduce 2-dimensionality in the crystal structure. The increase of the $A$-site disorder makes AFM(A) state unstable because of the decrease of structural anisotropy (2-dimensionality). On the other hand, it is advantageous to FM state generated by an isotropic double exchange interaction and it leads to FM state for PB32 and PB25. However, the effect of $\sigma^2$ is simultaneously enhanced by the $A$-site disorder and finally results in magnetic glassy state in the disordered form PB00. In conclusion the $A$-site randomness in Ba-based manganites clearly suppresses not only FM transition but also AFM(A) transition and leads to magnetic glassy state. We observed a similar randomness effect on Nd-compounds. Previously Akahoshi et al.\textsuperscript{11} reported somewhat different result of FM states as the ground state for Pr$_{0.5}$Ba$_{0.5}$MnO$_3$ and Nd$_{0.5}$Ba$_{0.5}$MnO$_3$. The present experiments suggest insufficient disorder in

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Table II. Refined structural parameters Pr-compounds (PB96$\sim$PB00) with various degrees of the $A$-site randomness. (See the text).

| Sample | PB57 | PB96 | PB32 | PB25 | PB00 |
|--------|------|------|------|------|------|
| Data Resource | Neutron | X-ray | Neutron | X-ray | X-ray |
| Space Group | $P4/mmm$ | $P4/mmm$ | $P4/mmm$ | $P4/mmm$ | $P4/mmm$ |
| $a$ (Å) | 3.909(1) | 3.909(2) | 3.9039(5) | 3.89989(5) | 3.89961(5) |
| $c$ (Å) | 7.7537(4) | 7.7547(5) | 7.75432(8) | 7.75891(1) | 7.76511(1) |
| $g$ | 0.982(1) | 0.984(2) | 0.939(2) | 0.854(2) | 0.783(2) |
| Pr/Ba at [ ] | $a$ | $b_{iso}=0.8(1)/0.5$ | $b_{iso}=0.9(1)/0.6$ | $b_{iso}=0.9(1)/0.6$ | $b_{iso}=0.9(1)/0.6$ |
| $b_{iso}=0.8(1)/0.5$ | $b_{iso}=0.9(1)/0.6$ | $b_{iso}=0.9(1)/0.9$ | $b_{iso}=0.9(1)/0.9$ | $b_{iso}=0.9(1)/0.9$ |
| $b_{iso}=0.9(1)/0.6$ | $b_{iso}=0.9(1)/0.9$ | $b_{iso}=0.9(1)/0.9$ | $b_{iso}=0.9(1)/0.9$ | $b_{iso}=0.9(1)/0.9$ |
| Mn | $z=0.246(7)$ | $z=0.246(3)$ | $z=0.247(2)$ | $z=0.247(1)$ | $z=0.247(1)$ |
| $z=0.246(3)$ | $z=0.246(3)$ | $z=0.247(2)$ | $z=0.247(1)$ | $z=0.247(1)$ |
| $z=0.247(2)$ | $z=0.247(1)$ | $z=0.247(1)$ | $z=0.247(1)$ | $z=0.247(1)$ |
| Pr/Ba at [ ] | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| O1 | $z=0.2386(4)$ | $z=0.2385(4)$ | $z=0.2391(8)$ | $z=0.2391(8)$ | $z=0.2391(8)$ |
| $z=0.2386(4)$ | $z=0.2385(4)$ | $z=0.2391(8)$ | $z=0.2391(8)$ | $z=0.2391(8)$ |
| $z=0.2385(4)$ | $z=0.2391(8)$ | $z=0.2391(8)$ | $z=0.2391(8)$ | $z=0.2391(8)$ |
| O2 | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ |
| $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ |
| $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ | $b_{iso}=0.8(1)/0.9$ |
| O3 | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ | $b_{iso}=0.5(1)/0.8$ |
| $R_{wp}$ (%) | 10.29 | 12.02 | 12.08 | 12.40 | 8.71 |
| $R_a$ (%) | 7.75 | 8.64 | 9.02 | 8.71 | 7.80 |
| $A$-site Order (%) | 96(2) | 87(4) | 70(4) | 57(6) | 0 |

The degree of $A$-site order ($S$) is defined by $(2g - 1) \cdot 100(\%)$, where $g$ is the refined occupancy factor represented as $[\Pr_{6-x}\ Ba_{1-g}]_{0}\ [\Pr_{1-g}\ Ba_{g}]_{1}\ Mn_{6}O_{9}; [\ p]$ and [ ]$_{0}$ show Pr-sites and Ba-sites in PrBa$Mn_{2}O_{6}$, respectively.
their samples.

Figure 11 shows temperature variation of electrical resistivity $\rho$ in (a) PB96, (b) PB32 and (c) PB00 at 0 and 5 T. For PB96 in which AFM(A) state is stable, magnetic field dependence of resistivity is little, although AFM(A) transition temperature is obviously suppressed by 18 K at 5 T. On the other hand, magnetoresistance (MR) effect is observed below $T_C$ ($= 158$ K) for ferromagnetic PB32 and below 120 K even for PB00 which has no long-range ferromagnetic order. The MR effects of these compounds at 5 T are summarized in Fig. 12, where MR(%) is given by $\text{MR(\%)} = (\rho(0) - \rho(H))/\rho(0) \times 100\%$ with $\rho(H)$ in 5 T and $\rho(0)$ in zero magnetic field. With increasing the $A$-site randomness, MR effect increases and the maximum MR effect reaches to 2360 % in PB00, although the temperature ($T_{MR}$) at the maximum MR effect decreases. It is obvious that the $A$-site randomness increases MR effect in Pr-compounds. This is the first observation of the efficient MR effect caused by the $A$-site disorder in a series of compounds with a fixed composition and various degrees of the $A$-site randomness. We also found very similar behaviors in Nd-compounds.

The decrease of resistivity below 150 K in PB32 is due to the development of FM state and the observed MR effect could be associated with the conversion of coexisted phases (AFM(A) phase or magnetic glassy phase) to FM phase by an external magnetic field. On the other hand PB00 shows no long range magnetic ordering nevertheless it shows similar behaviors of resistivity and MR effect. Such behaviors would be due to the development of short range magnetic ordering and the conversion of magnetic glassy phase to FM phase by an external magnetic field. At 2 K in PB00, a peculiar behavior, as shown in Fig. 13, has been observed. The resistivity decreases stepwise as the magnetic field increases, while the magnetization increases stepwise with the close relation to the resistivity behaviors. These behaviors are not reversible in the magnetic field. The stepwise behaviors in the magnetization and resistivity were observed up to 4.9 K but they vanished dramatically at 5.0 K. Similar behaviors were previously reported in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ doped with a few percent of other cations such as Sc, Ga or Co on the Mn site and were explained by an impurity induced-disorder, with the coexistence of several short-range AFI(CE) phases and small FM regions.$^{18,19}$ Our system has neither FM-to-AFI(CE) transition nor dopant in contrast to Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. A model based on ordinal two-phase mixture cannot explain the behavior. For instance, AFI(CE) phase in the coexistence with FM phase is continuously converted to FM phase as observed in LaBaMn$_2$O$_6$. We have no explanation for such multi-step magnetization and resistivity change at present. However we would like to emphasize a close relation between the observed behavior and any spatial
heterogeneity in a nanometer scale. Detailed study is now in progress.

§4. Summary

To summarize, we have investigated the structures and electromagnetic properties of the A-site disordered Ba-based manganite $R_{0.5}Ba_{0.5}MnO_3$ ($R = Y$ and rare earth elements) and compared $R_{0.5}Ba_{0.5}MnO_3$ with not only the A-site ordered manganite $RBaMn_2O_6$ but also ordinary disordered manganites $R_{0.5}A_{0.5}MnO_3$ ($A = Ca$ and Sr). The disordered form $R_{0.5}Ba_{0.5}MnO_3$ has a primitive cubic perovskite cell with no tilt of MnO$_6$ octahedra. The electronic states characteristic of perovskite manganites are absent in $R_{0.5}Ba_{0.5}MnO_3$ and magnetic glassy states govern the electronic state of $R_{0.5}Ba_{0.5}MnO_3$. The magnetic glassy states could be due to the disorder effect that hinders the long-range magnetic ordering and could occur as a result of the competition between randomly distributed ferromagnetic and antiferromagnetic interactions. The A-site randomness effect has been investigated in Pr-compounds with various degrees of Pr/Ba randomness at the A-sites. The A-site randomness suppresses both ferromagnetic and A-type antiferromagnetic transitions in $PrBaMn_2O_6$. On the other hand, magnetoresistance effect becomes remarkable with increase of the A-site disorder. As remarkable phenomena, multi-step magnetization and resistivity changes have been observed in $Pr_{0.5}Ba_{0.5}MnO_3$. Since the ionic radius of Ba$^{2+}$ is much larger than that of Sr$^{2+}$ and also $R^{3+}$, $R_{0.5}Ba_{0.5}MnO_3$ could include any spatial heterogeneity in a nanometer scale, which could be closely related to the multi-step magnetization and resistivity changes observed.

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