Structures and Electromagnetic Properties of New Metal-Ordered Manganites; \( \text{rBaMn}_2\text{O}_6 \) (\( \text{R} = \text{Y} \) and Rare Earth Elements)

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New metal-ordered manganites \( \text{rBaMn}_2\text{O}_6 \) have been synthesized and investigated in the structures and electromagnetic properties. \( \text{rBaMn}_2\text{O}_6 \) can be classified into three groups from the structural and electromagnetic properties. The first group (\( \text{R} = \text{La, Pr and Nd} \)) has a metallic ferromagnetic transition, followed by an A-type antiferromagnetic transition in \( \text{PrBaMn}_2\text{O}_6 \). The second group (\( \text{R} = \text{Sm, Eu and Gd} \)) exhibits a charge-order transition, followed by an antiferromagnetic long range ordering. The third group (\( \text{R} = \text{Tb, Dy and Ho} \)) shows successive three phase transitions, the structural, charge/orbital-order and magnetic transitions, as observed in \( \text{YBaMn}_2\text{O}_6 \). Comparing to the metal-disordered manganites \( \text{(rBa}_{0.5+x}\text{A}_{0.5})\text{MnO}_3 \), two remarkable features can be recognized in \( \text{rBaMn}_2\text{O}_6 \); (1) relatively high charge-order transition temperature and (2) the presence of structural transition above the charge-order temperature in the third group. We propose a possible orbital ordering at the structural transition, that is a possible freezing of the orbital, charge and spin degrees of freedom at the independent temperatures in the third group. These features are closely related to the peculiar structure that the \( \text{MnO}_2 \) square-lattice is sandwiched by the rock-salt layers of two kinds, \( \text{RO} \) and \( \text{BaO} \) with extremely different lattice-sizes.

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The magnetic and electrical properties of perovskite-type manganites with the general formula \( (\text{R}_{1-x}\text{A}_x)^{2+}\text{MnO}_3 \) (\( \text{R} = \) rare earth elements and \( \text{A} = \) alkaline earth elements) have been extensively investigated for the last decade [1]. Among the interesting features are the so-called colossal magnetoresistance (CMR) and metal-insulator (M-I) transition accompanied by charge and orbital ordering. It is now widely accepted that these enchanting phenomena are caused by the strong correlation/competition of multi-degrees of freedom, that is, spin, charge, orbital and lattice.

The structure of perovskite \( \text{RMnO}_3 \) consists of \( \text{MnO}_2 \) square-sublattice and \( \text{RO} \) rock-salt-sublattice. The mismatch between the larger \( \text{MnO}_2 \) sublattice and the smaller \( \text{RO} \) sublattice is relaxed by tilting and rotating \( \text{MnO}_6 \) octahedra, leading to the lattice distortion from cubic to, mostly, orthorhombic \( \text{GdFeO}_3 \)-type structure. At this lattice distortion, the bond angle \( \angle_{\text{MnO-Mn}} \) deviates from 180°, resulting in a significant change of an effective one-electron bandwidth (\( W \)) or equivalently \( e_g \)-electron transfer interaction (\( t \)). In the substitution system of \( (\text{R}_{1-x}\text{A}_x)^{2+}\text{MnO}_3 \) with a fixed \( x \) and a random distribution of \( \text{R}^{3+} \) and \( \text{A}^{2+} \), the structural and electromagnetic properties have been explained by the degree of mismatch, that is the tolerance factor \( f = (\langle r_A \rangle + r_O)/[\sqrt{2}(r_{\text{Mn}} + r_O)] \), where \( \langle r_A \rangle \), \( r_{\text{Mn}} \) and \( r_O \) are (averaged) ionic radii for the respective elements, because \( W \) or \( t \) is changed by varying \( f \).

Figure 1 shows the generalized phase diagram for \( (\text{rBa}_{0.5+x}\text{A}_{0.5})\text{MnO}_3 \) (Ref. 1). FM: ferromagnetic metal, AFM(A): A-type antiferromagnetic metal, AFI(CE): CE-type antiferromagnetic insulator, COI(CE): CE-type charger/orbital-ordered insulator, PM: paramagnetic metal.

FIG. 1: Generalized phase diagram for \( (\text{rBa}_{0.5+x}\text{A}_{0.5})\text{MnO}_3 \) (Ref. 1). FM: ferromagnetic metal, AFM(A): A-type antiferromagnetic metal, AFI(CE): CE-type antiferromagnetic insulator, COI(CE): CE-type charger/orbital-ordered insulator, PM: paramagnetic metal.

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0.975). In the middle region \((f \sim 0.975)\), the competition between the ferromagnetic DE and the antiferromagnetic CO interactions results in various phenomena including CMR.

Recently, it has been argued how the A-site randomness affect the physical properties of \((R_{1-x}A_x)^{2+}_3\)MnO\(_3\). The phenomena such as the coexistence of FM phase with CO phase and the electronic phase separation [2] may come from the A-site randomness. Unfortunately, almost all the works devoted to a series of perovskite-type manganites so far are on the disordered perovskite-type manganites with \(R^{3+}\) and \(A^{2+}\) ions being randomly distributed. This means that, whenever \(x\) is finite, there inevitably exists a disorder in the lattice. Since the physical properties of the manganite perovskite are quite sensitive to even a tiny change in lattice distortion, it is important to employ a compound without A-site disorder in order to make clear the effect of A-site randomness.

Very recently, we successfully synthesized a metal-ordered perovskite-type manganese YBaMn\(_2\)O\(_6\) with a successive stacking of YO-MnO\(_2\)-BaO-MnO\(_2\)-YO (see Fig. 2(a)) and observed successive three phase transitions; a structural transition without any charge and magnetic order at \(T_S = 520\) K, a CO transition (M-I transition) at \(T_{CO} = 480\) K and an antiferromagnetic transition at \(T_N = 195\) K [3]. The observed \(T_{CO} = 480\) K is the highest among the perovskite-type manganites. Across the phase transition at \(T_S = 520\) K, the resistivity shows little change and the magnetic susceptibility exhibits a large reduction. Furthermore the magnetic interaction seems to be changed from ferromagnetic above \(T_S\) to antiferromagnetic below \(T_S\). Such transition was first observed in the perovskite manganites. The expectation that such novel transition could be closely related to the metal-ordered structure drove us to the study of metal-ordered perovskite-type manganites RBA\(_{2}\)Mn\(_2\)O\(_6\). In this paper we report the synthesis, structures and physical properties of new metal-ordered perovskite-type manganites RBA\(_{2}\)Mn\(_2\)O\(_6\) with a successive stacking of RO-MnO\(_2\)-BaO-MnO\(_2\)-RO. We summarize the results as a phase diagram and we compare the obtained phase diagram with that of \((R^{3+}_{1-x}A^{2+}_x)^{3+}\)MnO\(_3\) shown in Fig. 1.

Powder samples were prepared by a similar solid-state reaction of \(R_2O_3\), BaCO\(_3\) and MnO\(_2\) to that used for YBaMn\(_2\)O\(_6\) [3]. The obtained products were checked to be single phases by X-ray diffraction. No perovskite-type compound was produced for Ce, Yb and Lu. The Er- and Tm-compounds included a significant amount of impurity phase.

The crystal structure was determined for 300-573 K by powder X-ray diffraction using CuK\(_\alpha\) radiation. The superlattice with a charge and orbital ordering was investigated by electron diffraction. The magnetic properties were studied using a SQUID magnetometer in a temperature range \(T = 5-700\) K under a magnetic field of 0.1 T. The electric resistivity of a sintered pellet was measured for \(T = 100-620\) K by a conventional four-probe technique.

The X-ray diffractions of all compounds clearly show the \((0,0,1/2)\)-reflection indexed with the simple cubic perovskite structure, which is an evidence for the same metal-ordered structure as that of YBaMn\(_2\)O\(_6\). The crystal structure at room temperature is tetragonal \((a_p \times a_p \times 2c_p)\) in La- and Pr-compounds, while in the compounds with \(R = Sm \sim Ho\) it has a larger cell \((\sqrt{2}a_p \times \sqrt{2}b_p \times 2c_p)\) as observed in YBaMn\(_2\)O\(_6\) [3], where \(a_p\), \(b_p\) and \(c_p\) denote the primitive cell for the simple cubic perovskite. The X-ray diffraction pattern of Nd-compound exhibits a mixture of \((a_p \times a_p \times 2c_p)\) and \((\sqrt{2}a_p \times \sqrt{2}b_p \times 2c_p)\)-phases at room temperature.

RBA\(_{2}\)Mn\(_2\)O\(_6\) can be classified into three groups from the obtained structural and electromagnetic properties. The first group RBA\(_{2}\)Mn\(_2\)O\(_6\) with \(R^{3+} = Ln^{3+}\), Pr\(^{3+}\) and Nd\(^{3+}\) has a FM transition at \(T_C\), followed by antiferromagnetic transitions in PrBaMn\(_2\)O\(_6\) (see Fig. 3(a)) and NdBaMn\(_2\)O\(_6\). The obtained \(T_C\) for LaBaMn\(_2\)O\(_6\) agrees well with the previous report [4]. The neutron magnetic diffraction study has revealed an A-type antiferromagnetic transition for PrBaMn\(_2\)O\(_6\) [5]. This is consistent with the relatively low resistivity below \(T_N\) compared with that in the CO state of EuBaMn\(_2\)O\(_6\) or DyBaMn\(_2\)O\(_6\), as shown in Fig. 3. A semiconductive behavior in the paramagnetic metallic (PM) state of PrBaMn\(_2\)O\(_6\) is due to loosely sintered samples. The second group consists of RBA\(_{2}\)Mn\(_2\)O\(_6\) with \(R^{3+} = Sm^{3+}\), Eu\(^{3+}\) and Gd\(^{3+}\). The compounds exhibit CO transitions, followed by antiferromagnetic long range ordering. Figure 3(b) shows a typical example of magnetic susceptibility and resistivity for EuBaMn\(_2\)O\(_6\). The third group includes the compounds with \(R^{3+} = Tb^{3+}\), Dy\(^{3+}\) and Ho\(^{3+}\) whose ionic radii are close to Y\(^{3+}\). These compounds show three phase transitions as observed in YBaMn\(_2\)O\(_6\) [3]. The magnetic susceptibility and resistivity of DyBaMn\(_2\)O\(_6\) are shown in Fig. 3(c) as an example. The distinct transitions at \(T_S\), \(T_{CO}\) and \(T_N\) are commonly observed in this series. The change of magnetic interac-

![FIG. 2: Crystal structure of YBaMn\(_2\)O\(_6\) (a) and a schematic illustration of structure for RBA\(_{2}\)Mn\(_2\)O\(_6\) (b). The MnO\(_2\)-square-lattice is sandwiched by the rock-salt layers of two kinds, RO and BaO with the different lattice-sizes.](image-url)
gram. Here we express the phase diagram as a function of magnetic susceptibility ($\chi$) and transition temperatures, respectively. DyBaMn$_2$O$_6$ magnetic, antiferromagnetic and charge/orbital-ordered transition without any charge and magnetic order at $T_S$ above $T_{CO}$ in $R$BaMn$_2$O$_6$ with the small ionic size of $R^{3+}$.

The results are summarized in Fig. 4 as a phase diagram. Here we express the phase diagram as a function of the ratio of ionic radius, $r_{R^{3+}}/r_{Ba^{2+}}$ [6], instead of $f$. In $R$BaMn$_2$O$_6$, the MnO$_2$ sub-lattice is sandwiched by the rock-salt layers of two kinds, RO and BaO with the different lattice-sizes, as shown in Fig. 2(b) and therefore the tolerance factor cannot be defined. The ratio, $r_{R^{3+}}/r_{Ba^{2+}}$, is a measure of mismatch between RO- and BaO-lattices.

It is very interesting to compare Fig. 4 with Fig. 1. Figure 4 is similar to Fig. 1 as a whole. There exist the characteristic phases such as the FM phase and the CO-type CO phase in both phase diagrams. In Fig. 1, the FM phase appears in La$_{0.5}$Sr$_{0.5}$MnO$_3$ with $f = 0.996$, which is defined in the average ionic size of La$^{3+}$(1.36 Å)/Sr$^{2+}$(1.44 Å) = 1.40 Å. In Fig. 4, on the other hand, the FM phase appears around $R = La$ and the CO state becomes dominant for Nd and later rare earth. Incidentally if a hypothetical tolerance factor $f'$ were calculated from the average ionic size of $R^{3+}/Ba^{2+}$, the FM phase would appear around $f' = 1.026$ (LaBaMn$_2$O$_6$) far beyond $f' = 1$ and the CO phase would be stable around $f' = 1$ (from $f' = 1.005$ for SmBaMn$_2$O$_6$ to $f' = 0.995$ for YBaMn$_2$O$_6$). In $R$BaMn$_2$O$_6$, the MnO$_2$ sub-lattice is sandwiched by RO and BaO layers with the different lattice-sizes and as a result the MnO$_6$ octahedron itself is distorted in a peculiar manner that the oxygen atoms of MnO$_2$ square-lattice are strongly bound by $R^{3+}$ resulting in a buckling of Mn and oxygen atoms in the MnO$_2$ square plane [7], in contrast to the rigid MnO$_6$ octahedra in $LaBaN_{0.5}$$_{0.5}$MnO$_3$. The ionic size of Ba$^{2+}$ (1.61 Å) [6] is much larger than those of Sr$^{2+}$ and all of $R^{3+}$. In the combination of $R^{3+}$/Ba$^{2+}$ the mismatch between RO- and BaO-lattices.

FIG. 3: Temperature dependence of resistivity and magnetic susceptibility ($\chi$) for (a) PrBaMn$_2$O$_6$, (b) EuBaMn$_2$O$_6$ and (c) DyBaMn$_2$O$_6$. $T_C$, $T_N$, and $T_{CO}$ represent the ferromagnetic, antiferromagnetic and charge/orbital-ordered transition temperatures, respectively. DyBaMn$_2$O$_6$ shows a structural transition without any charge and magnetic order at $T_S$ (see the text).

FIG. 4: Phase diagram for $R$BaMn$_2$O$_6$. The notation of each phase and transition temperature is the same as that defined in Fig. 1 and Fig. 3 (see the text). The PM’ is a paramagnetic metal with a possible orbital ordering (see the text). Comparing to the ($R^{3+}A_{0.5}^{2+}x$)MnO$_3$, two remarkable features can be recognized in $R$BaMn$_2$O$_6$: (1) relatively high $T_{CO}$ and (2) the presence of structural transition at $T_S$ above $T_{CO}$ in $R$BaMn$_2$O$_6$ with the small ionic size of $R^{3+}$.
is the smallest in La\(^{3+}\)/Ba\(^{2+}\). Therefore lattice distortion is expected to be a little in LaBaMn\(_2\)O\(_6\). Actually the structure of LaBaMn\(_2\)O\(_6\) is tetragonal and the FM phase appears as the ground state. Here it should be noticed again that PrBaMn\(_2\)O\(_6\) with the second smallest mismatch shows the FM to A-type antiferromagnetic metal (AFM) transition. A similar A-type AFM transition was previously reported in metal-disordered Pr\(_{0.5}\)Sr\(_{0.5}\)Mn\(_3\)O\(_7\) or Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) with \(f \approx 0.985\) [8]. Among the FM phases the \(T_C\) is little dependent of the ratio, \(r_{R^{3+}}/r_{Ba^{2+}}\). This suggests that the lattice distortion in PrBaMn\(_2\)O\(_6\) is not so considerable as the ferromagnetic interaction or DE interaction is influenced. Actually the Weiss temperature in the PM region above \(T_S\) is a ferromagnetic value about +300 K even in YBaMn\(_2\)O\(_6\) which has the largest lattice distortion. On the other hand, the CO state becomes stable as the ratio, \(r_{R^{3+}}/r_{Ba^{2+}}\) decreases. The \(T_{CO}\) increases across \(T_C\) around NdBaMn\(_2\)O\(_6\) and reaches the champion record \(T_{CO} = 480\) K in YBaMn\(_2\)O\(_6\). Our recent study of electron diffraction and neutron diffraction has revealed that YBaMn\(_2\)O\(_6\) has a CE-type charge and orbital order with a 4-fold periodicity along the c-axis \((2\sqrt{2}a \times 2\sqrt{2}b \times 4c_p)\) [9]. Taking the layer-type metal-order into the consideration, this new type of charge and orbital order (4-CE-type CO) can be explained as follows: the orbital ordered pattern within the a-b plane varies in the phase across the BaO- or YO-layer, that is \(aalpha beta\)-stacking along the c-axis, where the \(beta\)-type is derived from the interconversion of the \(d_{3z^2-r^2}\) and \(d_{4p^2-r^2}\) sublattices in the ordinary CE-type layer (alpha-type).

There are remarkable features in the phase diagram of RBA\(_2\)Mn\(_2\)O\(_6\): (1) the high \(T_{CO}\) and (2) the presence of structural transition at \(T_S\) above \(T_{CO}\). It is easy to understand the relatively high \(T_{CO}\) in RBA\(_2\)Mn\(_2\)O\(_6\), because the absence of randomness at A-site and the layer-type metal-order are favorable for the charge ordering of Mn\(^{3+}\)/Mn\(^{4+}\). Furthermore the phase diagram indicates that the increase of the mismatch between RO- and BaO-lattices also enhances the charge ordering. The structural transition at \(T_S\) is not accompanied by any charge and magnetic order but by the reduction of magnetic susceptibility. The temperature dependences of magnetic susceptibility suggest the change of magnetic interaction with Mn ions from ferromagnetic above \(T_S\) to antiferromagnetic below \(T_S\) [3]. Such novel transition is characteristic of the compounds with small ionic radii of R\(^{3+}\) in which the MnO\(_2\) square-lattice is sandwiched by two rock-salt layers with extremely different lattice-sizes. This situation introduces a strong frustration to the MnO\(_2\) sub-lattice and as a result the MnO\(_6\) octahedron itself is heavily distorted leading to a complex structural deformation (triclinic or monoclinic) [7]. Such deformation must give a new perturbation to the competition of multi-degrees of freedom among charge, orbital, spin and lattice, and affect the characteristic properties such as CMR and charge/orbital ordering. We propose a possible orbital ordering, presumably \(d_{x^2-y^2}\)-type orbital ordering, at \(T_S\), referring to the A-type AFM. We have obtained some evidence for the orbital ordering from the detailed structural investigation by X-ray and neutron diffraction [7]. The freezing of the orbital, charge and spin degrees of freedom at the independent temperatures, \(T_S\), \(T_{CO}\) and \(T_N\), could be closely related to the peculiar structure of the metal-ordered perovskite-type manganites, that is a layer type and a low symmetric structure, an asymmetric distortion of MnO\(_6\) octahedron and so on.

In the phase diagram of (R\(^{3+}\),A\(^{2+}\))MnO\(_3\), the middle region \((f \approx 0.975)\) where the ferromagnetic DE and the antiferromagnetic CO interactions compete each other is responsible for various phenomena including CMR. Such region may correspond to the solid solution between NdBaMn\(_2\)O\(_6\) and SmBaMn\(_2\)O\(_6\) or PrBaMn\(_2\)O\(_6\) in the phase diagram of RBA\(_2\)Mn\(_2\)O\(_6\). Actually rather complex behaviors have been observed in NdBaMn\(_2\)O\(_6\) [5]. Furthermore our preliminary experiments have revealed the successful synthesis of metal-disordered manganites (R\(^{3+}\),Ba\(^{2+}\))MnO\(_3\). The (R\(^{3+}\),Ba\(^{2+}\))MnO\(_3\) will give us a chance of quantitative discussion on the effect of A-site randomness.

In summary, new metal-ordered perovskite-type manganites RBA\(_2\)Mn\(_2\)O\(_6\) (\(R = Y\) and rare earth elements) have been synthesized and investigated in the structures and electromagnetic properties. The RBA\(_2\)Mn\(_2\)O\(_6\) can be classified into three groups from the obtained structural and electromagnetic properties. The first group \((R = La, Pr\) and Nd\) has a metallic ferromagnetic transition, followed by an A-type antiferromagnetic transition in PrBaMn\(_2\)O\(_6\). The second group \((R = Sm, Eu\) and Gd\) exhibits a CO transition, followed by an antiferromagnetic long range ordering. The third group \((R = Tb, Dy\) and Ho\) shows successive three phase transitions, the structural, CO and magnetic transitions, as observed in YBaMn\(_2\)O\(_6\). Comparing to metal-disordered (R\(^{3+}\),A\(^{2+}\))MnO\(_3\), there are two remarkable features in RBA\(_2\)Mn\(_2\)O\(_6\): (1) the relatively high charge-order transition temperature and (2) the presence of structural transition without any charge and magnetic order above the charge order temperature in the third group. We propose a possible orbital ordering at the structural transition, that is a possible freezing of the orbital, charge and spin degrees of freedom at the independent temperatures in the third group. These are closely related to the structural feature that the MnO\(_2\) sub-lattice is sandwiched by two kinds of rock-salt layers, RO and BaO with the different lattice-sizes and as a result the MO\(_6\) octahedron itself is distorted in a peculiar manner.

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