

Structures and physical properties of metal-ordered manganites RBaMn_2O_6 (R : Y and rare earth elements)

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Abstract

New metal-ordered manganites RBaMn_2O_6 with a successive stacking of $\text{RO-MnO}_2\text{-BaO-MnO}_2\text{-RO}$ have been synthesized and investigated in the structures and electromagnetic properties. Comparing to the metal-disordered manganites, two remarkable features are recognized in RBaMn_2O_6 : (1) relatively high charge-order transition temperature and (2) the presence of structural transition without any charge and magnetic ordering. These features are closely related to the peculiar structure that the MnO_2 square-lattice is sandwiched by the rock-salt layers of two kinds; RO and BaO with different lattice sizes.

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Recently, magnetic and electrical properties of perovskite-type manganites with a general formula $(\text{R}_{1-x}\text{A}_x^{2+})\text{MnO}_3$ (R = rare earth elements and A = alkaline earth elements) have been extensively investigated (see for reviews Ref. [1]). Almost all the works devoted to a series of perovskite-type manganites so far are on the disordered manganites with the R^{3+} and A^{2+} ions being randomly distributed. Since the physical properties of the perovskite-type manganites 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 manganite YBaMn_2O_6 with a successive stacking of $\text{YO-MnO}_2\text{-BaO-MnO}_2\text{-YO}$ (see the inset in Fig. 2) and observed following three-phase transitions: a structural transition at $T_S = 520$ K, a charge-order (CO) transition at $T_{CO} = 480$ K and an antiferromagnetic transition at $T_N = 195$ K [2]. Across the phase transition at T_S the resistivity shows little change, whereas the magnetic susceptibility drops significantly and the

magnetic interaction which estimates from the Curie-Weiss fitting varies from ferromagnetic above T_S to antiferromagnetic below T_S . Such transition was first observed in the perovskite-type manganites. In this paper, we report the synthesis, structures and physical properties of new metal-ordered manganites RBaMn_2O_6 (R : Y and rare earth elements).

Powder samples were prepared by a solid-state reaction of R_2O_3 , BaCO_3 and MnO_2 [2]. The synthesis of compounds with Ce, Yb and Lu was completely failed. The Er- and Tm-compounds included a significant amount of impurity phase.

The crystal structures were determined by powder X-ray diffraction using $\text{Cu K}\alpha$ radiation. The magnetic properties were studied using a SQUID magnetometer. The electric resistivity of the sintered pellets was measured by a conventional four-probe technique.

RBaMn_2O_6 can be classified into three groups from the electromagnetic properties. The first group includes the compounds with R = Tb^{3+} , Dy^{3+} and Ho^{3+} whose ionic radii are close to Y^{3+} . These compounds show successive three-phase transitions as observed in YBaMn_2O_6 . The magnetic susceptibility and resistivity of $\text{DyBaMn}_2\text{O}_6$ are shown in Fig. 1. Although the reduction of magnetic susceptibility across T_S is clearly observed, it is difficult to read ferromagnetic to

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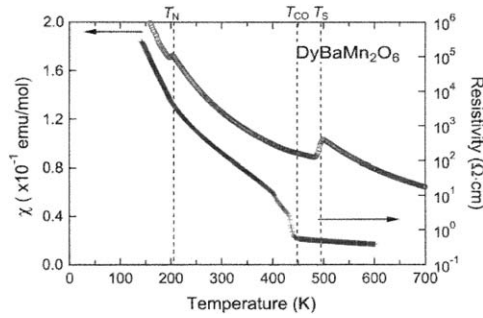


Fig. 1. Magnetic susceptibility and electrical resistivity as a function of temperature for DyBaMn₂O₆.

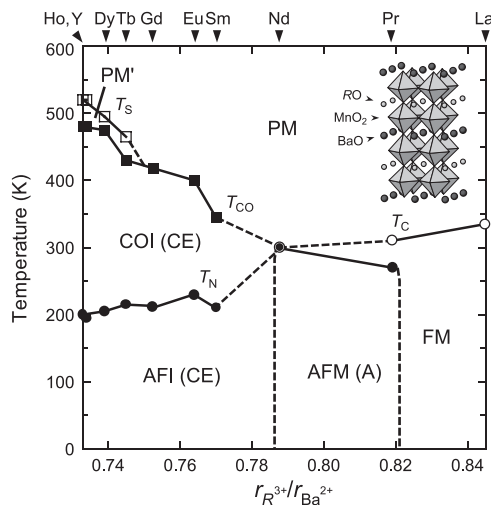


Fig. 2. Phase diagram for metal-ordered manganites RBaMn₂O₆ (R = Y and rare earth elements). PM: paramagnetic metal, FM: ferromagnetic metal, AFM(A): A-type antiferromagnetic metal, COI(CE): CE-type charge- and orbital-ordered insulator, AFI(CE): CE-type antiferromagnetic insulator.

antiferromagnetic change of magnetic interaction between Mn ions, because of the significant contribution of magnetic rare earth ions to the total magnetic susceptibility. However, the distinct transitions at T_S and T_{CO} are commonly observed in this series. The second group RBaMn₂O₆ with R = La, Pr and Nd has metallic ferromagnetic transition at T_C followed by the A-type antiferromagnetic transition in PrBaMn₂O₆ and NdBaMn₂O₆. The third group consists of the intermediate R = Sm, Eu and Gd, and exhibits the structural and CO transitions simultaneously, followed by the magnetic long-range ordering.

The results are summarized in Fig. 2 as a phase diagram. It is very interesting to compare the obtained phase diagram to the generalized phase diagram of the

metal-disordered (R_{0.5}A_{0.5})MnO₃ which is expressed as a function of the tolerance factor (f) [1]. The generalized phase diagram is expressed as a function of the tolerance factor (f), where the ferromagnetic metallic (FM) state appears near $f \sim 1$, the CO state is most stabilized for $f < 0.975$ and the middle region ($f \sim 0.975$) is responsible for various phenomena including CMR.

In the metal-ordered RBaMn₂O₆, however, the tolerance factor cannot be defined because the MnO₂ square-lattice is sandwiched by the rock-salt layers of two kinds: RO and BaO with different lattice sizes. Hence we express the phase diagram as a function of the ratio of ionic radius: $r_{R^{3+}}/r_{Ba^{2+}}$.

The phase diagram of RBaMn₂O₆ is similar to the generalized phase diagram as a whole. There exist the characteristic phases such as FM phase due to double-exchange interaction and CE-type CO phase. However, there are two striking features in the phase diagram of RBaMn₂O₆: (1) the high T_{CO} and (2) the presence of structural transition at T_S above T_{CO} . The FM state appears around R = La and the CO state is more stable for Nd and later rare earth. The T_{CO} increases with decreasing the ratio of $r_{R^{3+}}/r_{Ba^{2+}}$ and reaches the champion record $T_{CO} = 480$ K in YBaMn₂O₆. The relatively high T_{CO} in the metal-ordered manganites is easily understood because the metal order at A-site is favorable for the charge ordering of Mn³⁺/Mn⁴⁺. The phase transition at T_S is not accompanied by any charge ordering and magnetic ordering but by the reduction of magnetic susceptibility and the change of magnetic interaction from ferromagnetic to antiferromagnetic. This transition is characteristic of the compounds with small ionic radii of R³⁺ in which the MnO₂ square-lattice is sandwiched by two rock-salt layers with the extremely different lattice sizes. This situation introduces a strong frustration to the MnO₂ sub-lattice and as a result MnO₆ octahedron itself is distorted leading to a complex structural deformation (triclinic or monoclinic). Such deformation must give a new perturbation to the competition of multi-degrees of freedom, that is, spin, charge, orbital and lattice. We propose a possible orbital ordering, presumably $d_{x^2-y^2}$ -type orbital ordering, at T_S . The freezing of the orbital, charge and spin degrees of freedom at the independent temperatures might be closely related to the peculiar structure of the metal-ordered perovskite-type manganites.

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