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The A-site ordered manganese perovskite and its colossal magnetoresistance

Yutaka Ueda*, Tomohiko Nakajima

Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

Abstract

The A-site ordered manganites show the charge/orbital order (CO) transition far above room temperature. By using this advantage, we have engaged in the realization of colossal magnetoresistance (CMR) at room temperature by introducing some sophisticated disorders to $SmBaMn_2O_6$. The inter-site disorder of Sm/Ba results in no significant magnetoresistance (MR) effect. The La-substitution for both Sm- and Ba-sites is effective to realize MR effect. At room temperature and 9 T, we have achieved the record of MR effect about 340% in the sintered $Sm_{0.90}La_{0.24}Ba_{0.86}Mn_2O_6$. In a single crystal of the compound, the perfect CO insulator to ferromagnetic metal (FM) transition is observed at 9 T, showing the room temperature CMR over 1000%. TEM study reveals that the formation of microdomains with CO and FM or magnetic glassy states is crucial for CMR.

Keywords: A-site ordered manganite; Charge/orbital order; Colossal magnetoresistance; Randomness effect

1. Introduction

The magnetic and electrical properties of perovskite manganites with the general formula $(R^{3+}_{1-x}A^{2+}_x)MnO_3$ (R = rare earth elements; A = Ca and Sr) have been extensively investigated for the last several decades [1]. Among the interesting features are the so-called colossal magnetoresistance (CMR) and metal–insulator transition accompanied by charge/orbital order (CO). It is now widely accepted that these enchanting phenomena are caused by the strong

* Corresponding author. Tel.: +81 3 3478 8459; fax: +81 4 7136 3435.
E-mail address: yueda@issp.u-tokyo.ac.jp (Y. Ueda).

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correlation/competition among spin, charge and orbital degrees of freedom and such correlation is significantly influenced by the random distribution of R- and A-cations at the A-site. Recently the A-site ordered manganites, $RBaMn_2O_6$, have been successfully synthesized and its structures and electromagnetic properties have been reported [2–14]. As schematically shown in Fig. 1, the most significant structural feature of $RBaMn_2O_6$ is that the MnO_2 square sublattice is sandwiched by two types of rock-salt layers, RO and BaO, with much different sizes, and consequently the MnO_6 octahedron itself is distorted in a peculiar manner that both Mn and oxygen atoms in the MnO_2 plane are displaced toward the RO layer, in contrast to the rigid MnO_6 of the A-site disordered manganite $(R_{1-x}A_x)MnO_3$. This means that the structural and physical properties of $RBaMn_2O_6$ can be no longer explained in terms of the basic structural distortion, the so-called tolerance factor f, as in $R_{0.5}A_{0.5}MnO_3$. Fig. 2 shows the electronic phase diagram of $RBaMn_2O_6$ expressed as a function of the ratio of ionic radius of the A-site cations, $r_{R^{3+}}/r_{Ba^{2+}}$ [4,9,11–14]. Compared with the A-site disordered $R_{0.5}A_{0.5}MnO_3$, $RBaMn_2O_6$ displays remarkable features as follows:

(1) The CO transition temperatures (T_{CO}) are relatively high, which could be due to the absence of A-site randomness.
(2) The CO manner in the CE-type CO insulator (COI(CE)) phase has a new stacking variation of the in-plane CE-type CO with a fourfold periodicity along the c-axis, which could be due to a layer-type order of R and Ba. Furthermore, this CO manner changes into a new type with a twofold periodicity along the c-axis in the CE-type CO antiferromagnetic insulator (AFI(CE)) phase, although the spin structure has a new CE-type with a fourfold periodicity along the c-axis.
(3) There exists a structural transition at T_t above T_{CO} in $RBaMn_2O_6$ ($R = Tb \sim Y$), which is possibly accompanied by the $d_{x_2-y_2}$ type orbital order.
(4) $LaBaMn_2O_6$ shows a fractional transition from ferromagnetic metal (FM) to AFI(CE), which would be due to the decrease of bandwidth related to the increase of Mn–O distance.
(5) The critical behaviors such as the lowering of transition temperatures (T_C and T_{CO}) and FM-to-AFI(CE) transition responsible for CMR are absent in the phase boundary between FM and COI(CE), which also could be due to the absence of A-site randomness.

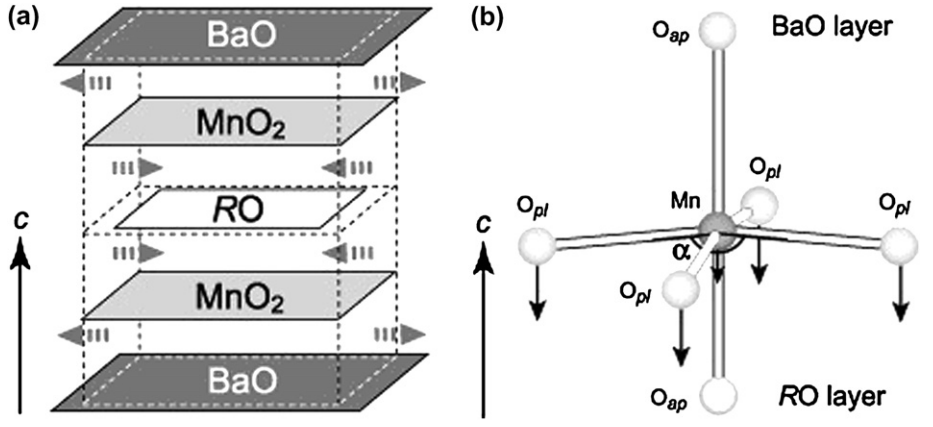

Fig. 1. (a) A schematic drawing of the structure for the A-site ordered manganite $RBaMn_2O_6$, and (b) an illustration of the distorted MnO_6 octahedron.