Successive phase transitions in a metal-ordered manganite perovskite YBaMn$_2$O$_6$

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Abstract

Structural, magnetic and electric properties of a metal-ordered perovskite YBaMn$_2$O$_6$ have been studied by means of powder X-ray diffraction, differential scanning calorimetric, magnetic susceptibility, and electric resistivity. It is found that this material undergoes a first-order structural phase transition at $T_{c1} = 520$ K, from a pseudo orthorhombic (monoclinic) phase ($T_{c1} < T$) to a pseudo tetragonal (monoclinic) one ($T < T_{c1}$). Accompanied by this transition the susceptibility exhibits a sharp drop where ferromagnetic exchange interaction becomes antiferromagnetic. Furthermore, two more transitions, a metal–insulator transition at $T_{c2} = 480$ K and an antiferromagnetic ordering at $T_{c3} = 200$ K, have been observed, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recently, magnetic and electric properties of manganite perovskite with a general formula $(A_{1-x}^{3+}A_x'^{2+})MnO_3$, where A^{3+} and A'^{2+} represent rare earth and alkaline earth ions, respectively, have been extensively investigated. Among the interesting features are the so-called colossal magnetoresistance observed in, e.g. La$_{0.7}$Sr$_{0.3}$MnO$_3$ [1] and metal–insulator (M–I) transition accompanied by charge and orbital ordering observed in, e.g. Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ [2]. 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 itself [3,4].

Unfortunately enough, almost all the works devoted to the series of manganite perovskite so far are on the disordered perovskite with the A^{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 [5] it is desirable to employ 'cleaner' compound in order to understand the effect of A-site disorder more systematically.

When x equals to 0.5, one can overcome this problem by preparing a metal-ordered double perovskite AA'Mn$_2$O$_6$ the structure of which consists of alternate stack of the A^{3+} and A'^{2+} ions along the c-axis as shown in Fig. 1. As far as the authors know only the ordered LaBaMn$_2$O$_6$ was reported [6]. In this work, we successfully prepared the ordered YBaMn$_2$O$_6$ and investigated the relation between structural and physical properties of this material.

2. Experimental

The synthesis of the ordered perovskite requires several complex processes as described in Refs. [7,8]. Starting materials Y$_2$O$_3$, MnO$_2$, and BaCO$_3$ were ground thoroughly, pressed into pellets and calcined in an Ar flow at 1300 °C for 48 h which yields the ordered YBaMn$_2$O$_{6-y}$ ($y \sim 0.9$) with a large amount of oxygen vacancy in the YO layer. Then, annealing it in flowing O$_2$ at 500 °C for 48 h leads to the fully oxidation of the sample, i.e. to $y \rightarrow 0$.

Thermogravimetric reduction in H$_2$ confirmed the oxygen content of the sample to be ideal stoichiometry O$_{6.0}$. The crystal structures were determined for 300–573 K by powder X-ray diffraction using Cu K$_\alpha$ radiation. Differential scanning calorimetric (DSC) measurements was carried out for 150–600 K. The heating/cooling rate was typically 5–20 K/min.

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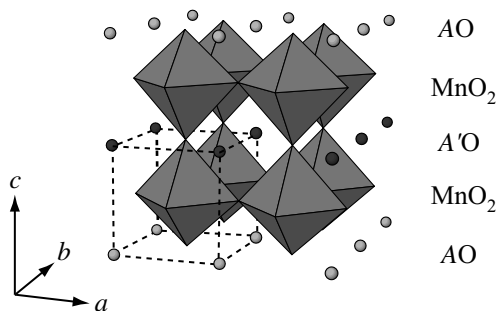 *E-mail address:* t-nakaji@issp.u-tokyo.ac.jp (T. Nakajima).

Fig. 1. Crystal structure of the ordered $AA'Mn_2O_6$. The broken lines represent the unit cell for the simple perovskite ($a_p \times b_p \times c_p$).

The magnetic properties were studied using a SQUID magnetometer in a temperature range $T = 5$–600 K in a magnetic field of 1000 Oe. The electric resistivity ρ of a sintered pellet was measured for $T = 100$–620 K by a conventional four-probe technique.

3. Results and discussion

The X-ray diffraction profile scanned at room temperature (Fig. 2(a)) indicates that the obtained sample is a mixture of a main phase of the ordered $YBaMn_2O_6$ and a miner impurity phase of $BaMnO_{3-\delta}$ (about 3%). The (001) reflection

around $2\theta = 12°$ assures the successful alternation of Y^{3+} and Ba^{2+} cations along the c-axis, thus doubling the c parameter with respect to the simple perovskite. It appears that the crystal structure is tetragonal but the careful analysis of the data finally led to the conclusion that it is monoclinic with the unit cell $a_p \times b_p \times 2c_p$, where a_p, b_p, and c_p represent lattice parameters for the simple perovskite structure. The structural parameters are determined as follows: $a = 3.901(9)$ Å, $b = 3.898(1)$ Å, $c = 7.602(2)$ Å, $\beta = 90.2(1)°$, and $V = 115.5(9)$ Å^3.

Fig. 3 shows the temperature dependence of the structural parameters where a clear jump is observed at $T_{c1} = 520$ K, suggesting a first-order transition. The nature of the first-order phase transition at T_{c1} is also visible in the DSC curve (Fig. 4) where a huge endothermic peak is observed on heating. We found that the structure of the high-T phase is also consistent with the monoclinic symmetry with the unit cell of $a_p \times b_p \times 2c_p$. The structural parameters, for example, at 573 K are determined as follows: $a = 3.930(6)$ Å, $b = 3.846(3)$ Å, $c = 7.731(2)$ Å, $\beta = 90.2(8)°$, and $V = 116.9(8)$ Å^3. It is strange that the high-T phase with a pseudo orthorhombic structure ($a > b$, $\beta \approx 90°$) has apparently a lower symmetry than the low-T phase with a pseudo tetragonal structure ($a \approx b$, $\beta \approx 90°$). We suppose the low-T phase may have superstructures originating from the charge/orbital ordering.

The careful reading of the DSC curve in Fig. 4 suggests that besides the already-mentioned peak at T_{c1} there are two
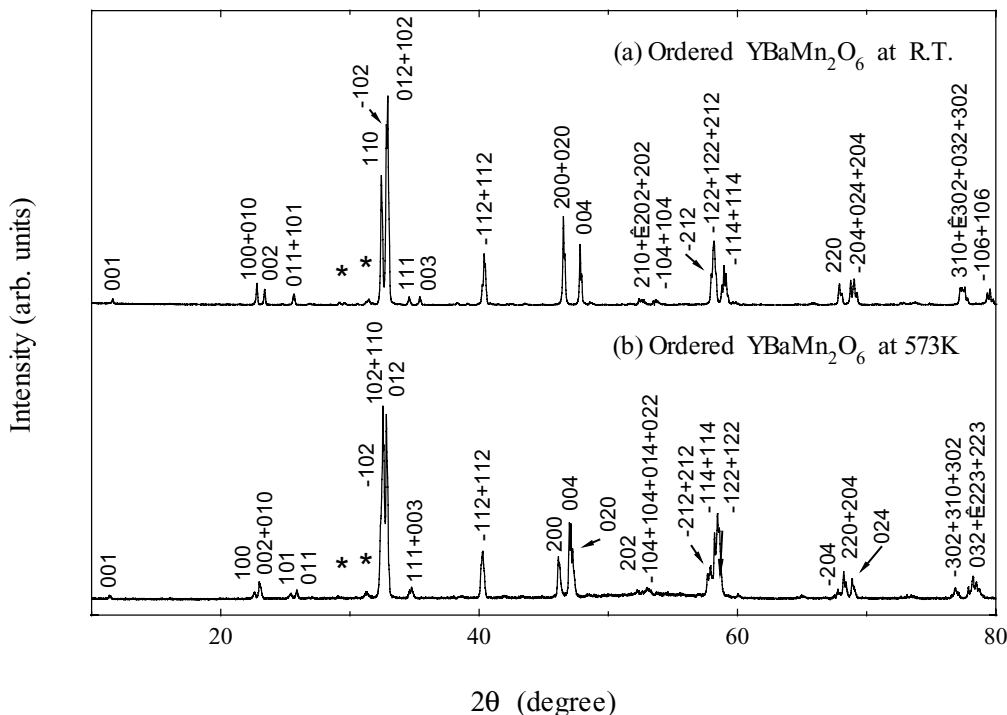

Fig. 2. X-ray diffraction data for the ordered $YBaMn_2O_6$ at: (a) RT and (b) 573 K. Both profiles can be indexed by assuming a monoclinic structure with the $a_p \times b_p \times 2c_p$ unit cell. Peaks marked by asterisks come from an impurity phase $BaMnO_{3-\delta}$ and Y_2O_3.
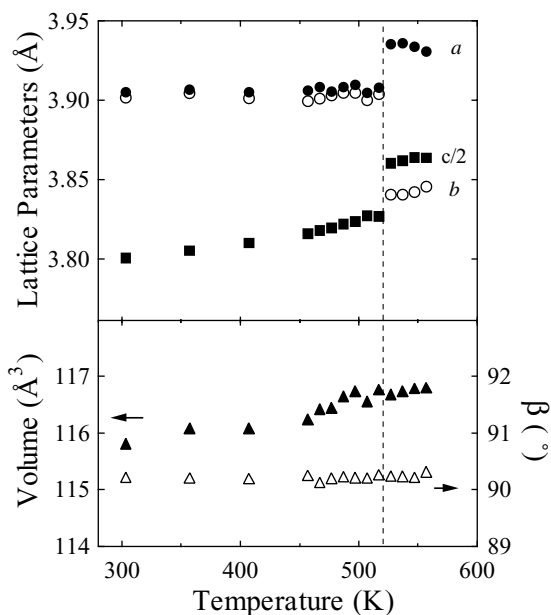
Fig. 3. Temperature variation of the reduced cell parameters a, b, $c/2$, β, and V for the ordered YBaMn$_2$O$_6$.

Fig. 5. Magnetic susceptibility and electric resistivity of the ordered YBaMn$_2$O$_6$ as a function of temperature.

weak endothermic peaks at $T_{c2} = 480$ K and $T_{c3} = 200$ K. In Fig. 5, we demonstrate the electric resistivity as a function of T, which can be characterized by the M–I transition that occurs at T_{c2} and by small anomalies at T_{c1} and T_{c3}. Although ρ for $T_{c2} < T$ decreases with increasing T, it should be essentially metallic considering the relatively low and constant resistivity ($\sim 10^{-1}$ Ω cm) and the fact that we used polycrystalline sample not a single crystal.

Also shown in Fig. 5 is the temperature dependence of the magnetic susceptibility χ measured at 1000 Oe. At high temperature above T_{c1} the χ–T curve shows a paramagnetic behaviour obeying the Curie–Weiss law with the effective
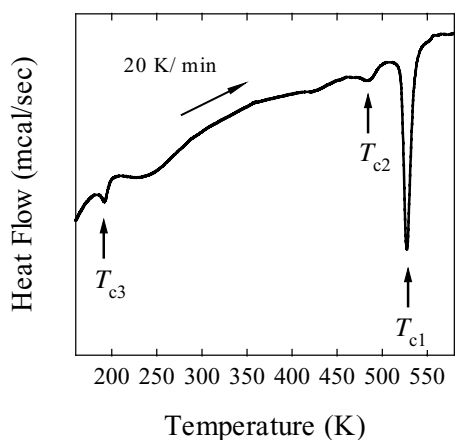

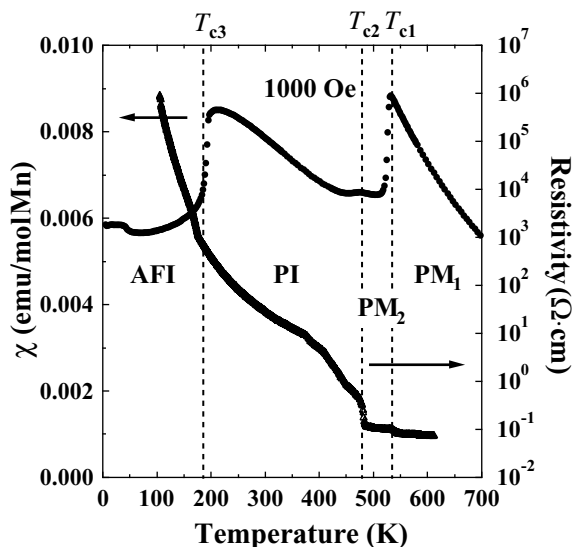Fig. 4. DSC curve of the ordered YBaMn$_2$O$_6$ upon heating with a speed of 20 K/min.

moment $P_{\mathrm{eff}} = 8.06\mu_{\mathrm{B}}$ and the Weiss constant $\theta_1 = 286$ K. The positive value of θ_1 suggests the ferromagnetic spin correlation and the value of P_{eff} is compatible with a theoretical value of $7.94\mu_{\mathrm{B}}$ derived from [Mn^{3+} + Mn^{4+}] in YBaMn$_2$O$_6$. Upon decreasing T, χ drops sharply at T_{c1} while only small anomaly is observed at T_{c2} where the M–I transition occurs. Below T_{c2} the χ–T curve once again shows a paramagnetic behaviour but the Curie–Weiss fitting gave a negative value of $\theta_2 = -379$ K, indicating an antiferromagnetic interaction. Finally, χ exhibits a steep drop at T_{c3} then reaching a constant value ~ 0.006 emu/mol Mn. Considering the negative value of θ_2, it is natural to assume that the transition at T_{c3} would be due to the antiferromagnetic long-range order.

As mentioned earlier, the ordered YBaMn$_2$O$_6$ shows three transitions namely from the paramagnetic metal with the nearly orthorhombic structure (PM$_1$) to the paramagnetic metal with the nearly tetragonal structure (PM$_2$) at T_{c1} then to the paramagnetic insulator (PI) at T_{c2} and finally to the antiferromagnetic insulator (AFI) at T_{c3}. Now let us discuss the successive phase transitions from the viewpoint of multi-degrees of freedom. The PM$_1$ state with the positive θ implies that the dominant ferromagnetic interactions at high temperatures originate from the double-exchange mechanism. Accordingly, without the transitions at T_{c1} and T_{c2} this compound would experience the ferromagnetic ordering. What we would like to emphasize is that in YBaMn$_2$O$_6$ the charge/orbital ordering occurs at much higher temperature compared with the disordered perovskite. Take Sm$_{0.5}$Ca$_{0.5}$MnO$_3$ [9] and Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ [2] for example the charge/orbital ordering temperature is reported to be, respectively, 270 and 140 K. This suggests that the disorder in the lattice originating from the random

distribution of A and A' cations significantly lowers the charge/orbital ordering temperature.

It has been known that the charge/orbital ordering is usually accompanied by the structural phase transitions as is seen in Ref. [10]. In the present compound however charge/orbital ordering temperature (T_{c2}) is lower than the structural phase transition (T_{c1}). This is significantly different from the transitions reported in the disordered manganite perovskite so far.

To fully understand the nature of the successive phase transition in particular intermediate phase (PM$_2$) it is necessary to perform microscopic measurements such as neutron diffraction and NMR, which are now in progress.

4. Conclusion

In summary, we studied the structural and physical properties of the ordered manganite YBaMn$_2$O$_6$ to find three phase transitions at $T_{c1} = 520$ K(PM$_1 \rightarrow$ PM$_2$), at $T_{c2} = 480$ K(PM$_2 \rightarrow$ PI) and at $T_{c3} = 200$ K(PI $\rightarrow$ AFI). At T_{c1} the structure changes from pseudo orthorhombic to pseudo tetragonal one. The M–I transition which occurs at T_{c2} would be accompanied by the charge/orbital ordering. Reflecting the ordering between Y^{3+} and Ba^{2+} ions the transition temperature is much higher than that reported for disordered manganite. The antiferromagnetic ordering occurs at T_{c3}.

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