Structures and Magnetic Properties of Tm1-yYyMn1-xCoxO3

Structures and Magnetic Properties of $Tm_{1-y}Y_yMn_{1-x}Co_xO_3$

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Abstract

The structure and magnetic properties of $Tm_{1-y}Y_yMn_{1-x}Co_xO_3$ with $0 \leqq x \leqq 0.5$ and $0 \leqq y \leqq 0.3$ were investigated by X-ray diffraction, specific heat and magnetization measurements. Thulium manganite $TmMnO_3$ prepared by solid-state synthesis at ambient pressure is hexagonal and antiferromagnetic with a Nèel temperature T_N of 86 K. The substitution of Y for Tm in $TmMnO_3$ does not greatly affect the fundamental hexagonal structure. The magnetization and specific heat measurement results for $Tm_{1-y}Y_yMnO_3$ can be qualitatively explained in terms of the dilution effect of Tm by Y. On the other hand, the structure of $TmMn_{1-x}Co_xO_3$ changes gradually from hexagonal to orthorhombic with the substitution of Co for Mn; hexagonal and orthorhombic phases coexist in samples for $x \leqq 0.3$ whereas $TmMn_{0.6}Co_{0.4}O_3$ is almost a single orthorhombic phase. The magnetization of $TmMn_{0.6}Co_{0.4}O_3$ in a field of 250 Oe increases rapidly at about 60 K with decreasing temperature. The difference between zero-field-cooled (ZFC) and field-cooled (FC) magnetizations increases remarkably at about 60 K. Moreover, the temperature dependences of the ZFC and the FC magnetizations exhibit peaks at about 40 and 30 K, respectively. Thus, $TmMn_{1-x}Co_xO_3$ exhibits complex magnetic properties.

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I. INTRODUCTION

Manganese oxides $R\mathrm{MnO_3}$ and cobalt oxides $R\mathrm{CoO_3}$ (R = rare earth) have been extensively investigated because of their diverse physical properties and their potential applications. $\mathrm{TmMnO_3}$ synthesized at ambient pressure is a hexagonal multiferroic compound [1, 2]. Orthorhombic $\mathrm{TmMnO_3}$ has been prepared under high pressures [3]. Ferroelectricity in this material has been reported to be induced by collinear magnetic order [4]. Synthesis of orthorhombic $\mathrm{TmCoO_3}$ under high pressures has been reported, and a structural study by using high-resolution neutron diffractometry has been performed at room temperature [5], but its physical properties have not been characterized. In the present study, we investigate the structures and the magnetic properties of $\mathrm{Tm_{1-y}Y_yMn_{1-x}Co_xO_3}$ for various x and y.

II. EXPERIMENTS AND DISCUSSION

Polycrystalline samples were prepared from the corresponding powder oxides $\mathrm{Tm_2O_3}$, $\mathrm{Mn_2O_3}$, and $\mathrm{Co_3O_4}$ in an $\mathrm{O_2}$ atmosphere by a conventional solid-state reaction. An X-ray diffraction (XRD) analysis was performed using Cu-Kα radiation and a graphite monochromator at room temperature. The XRD patterns were refined by using RIETAN-2000 [6]. Specific heat and magnetization measurements were, respectively, performed using a physical property measurement system (PPMS; Quantum Design) and a magnetic property measurement system (MPMS; Quantum Design). We measured the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations in a field of 250 Oe for all samples and the isothermal magnetizations at various temperatures for $\mathrm{TmMn_{0.6}Co_{0.4}O_3}$.

$\mathrm{Tm_{1-y}Y_yMn_{1-x}Co_xO_3}$ compounds for $y = 0 \sim 0.3$ and $x = 0 \sim 0.5$ were prepared in the present study. All the XRD patterns of $\mathrm{Tm_{1-y}Y_yMnO_3}$ compounds in which Y is substituted for Tm correspond to the same hexagonal space group of $\mathrm{P6_3cm}$ as $\mathrm{TmMnO_3}$. The temperature dependences of the ZFC and the FC magnetizations of $\mathrm{Tm_{1-y}Y_yMnO_3}$ are similar to those of $\mathrm{TmMnO_3}$, which exhibit Curie-Weiss behavior above 100 K, although the magnetization decreases slightly with increasing y. These results can be qualitatively explained by the dilution of Tm by Y.

Figure 1 shows XRD patterns of $\mathrm{TmMn_{1-x}Co_xO_3}$ for $x = 0 \sim 0.5$. $\mathrm{TmMnO_3}$ is a well-crystallized polycrystalline sample with a space group of $\mathrm{P6_3cm}$. When Co is substituted for

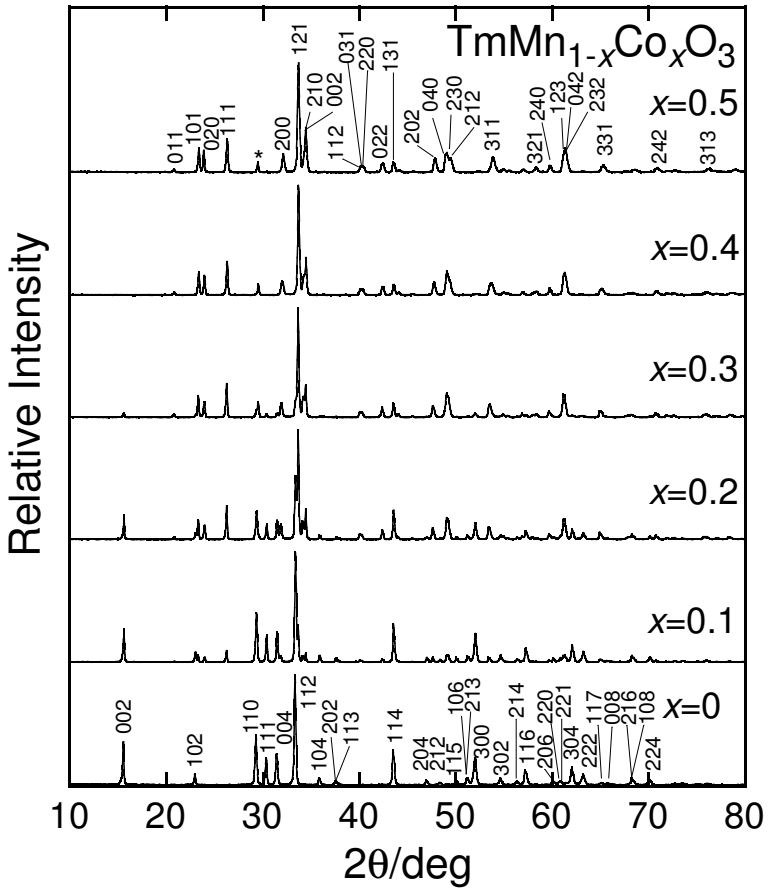

FIG. 1: X-ray diffraction patterns of $TmMn_{1-x}Co_xO_3$ for $x = 0 \sim 0.5$. The asterisk indicates a diffraction peak due to residual Tm_2O_3.

Mn, Bragg peaks indexed by an orthorhombic structure with a space group of Pnma are observed in addition to those for a hexagonal structure. $TmMn_{0.6}Co_{0.4}O_3$ and $TmMn_{0.5}Co_{0.5}O_3$ seem to exhibit a nearly single orthorhombic phase, except for impurities such as Tm_2O_3.

Figures 2 shows the temperature dependence of the specific heat divided by the temperature, and Fig. 3 shows the temperature dependences of the ZFC and FC magnetizations for $TmMn_{1-x}Co_xO_3$. The two peaks at 9.3 K and about 80 K for $TmMnO_3$ in Fig. 2 correspond to the Schottky anomaly of Tm^{3+} and the antiferromagnetic ordering of Mn ions [2], respectively. The ZFC and FC magnetization curves of $TmMnO_3$ in Fig. 3 resemble those in Ref. [1]; the difference between them $\Delta M = M_{\rm FC} - M_{\rm ZFC}$ increases gradually at temperatures below about 90 K with decreasing temperature for the antiferromagnetic ordering of $TmMnO_3$.

For $TmMn_{1-x}Co_xO_3$, the temperature of the peak of the Schottky anomaly shifts to lower

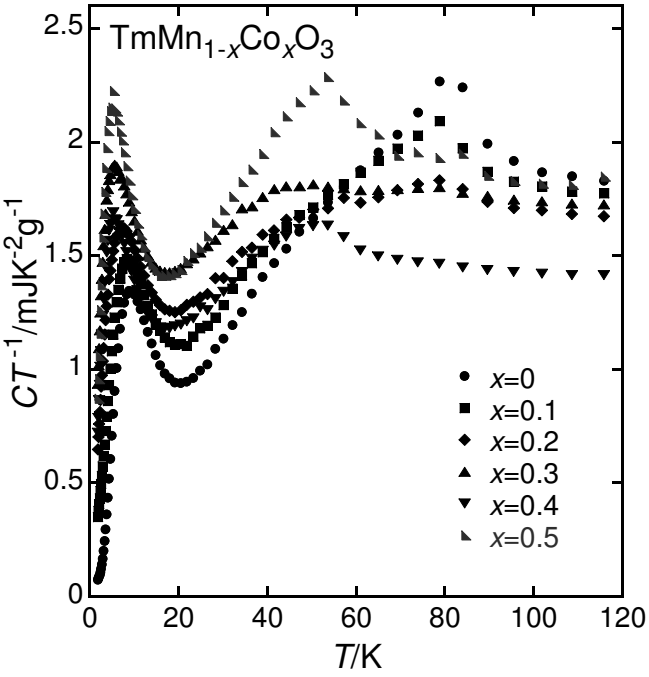

FIG. 2: Temperature dependence of C/T for $TmMn_{1-x}Co_xO_3$ with $x = 0 \sim 0.5$.

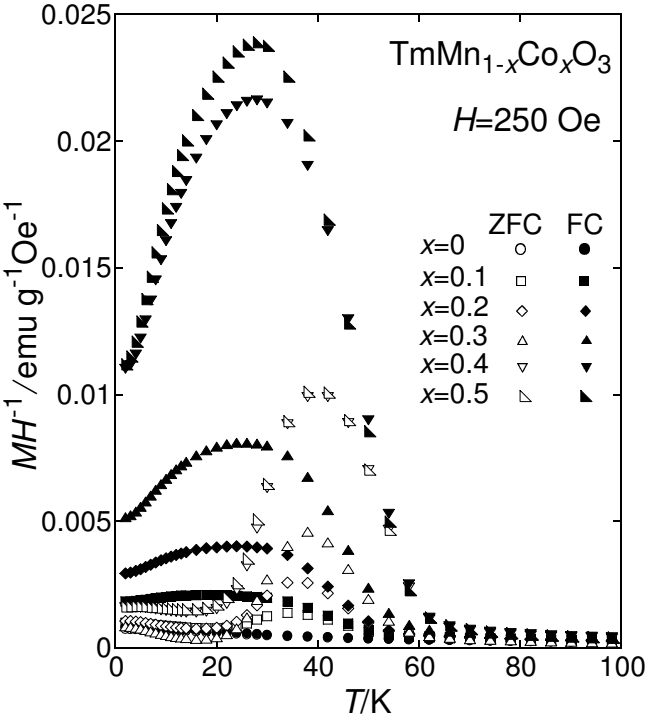

FIG. 3: Temperature dependence of M/H in a field of 250 Oe for $TmMn_{1-x}Co_xO_3$ with $x = 0 \sim 0.5$.

temperature with increasing x. This implies that the energy level splitting of Tm^{3+} increases with increasing substitution of Co for Mn. The peak at around 80 K in Fig. 2 decreases with increasing x; it disappears for $x = 0.4$ and is replaced by a new peak at around 50 K. On the other hand, the ZFC and the FC magnetizations both increase rapidly at about 60 K with decreasing temperature and exhibit peaks at about 40 and 30 K, respectively. The new peak of the specific heat at around 50 K and the rapid increase in the magnetization at temperatures below about 60 K indicate the appearance of a ferromagnetic order in orthorhombic $TmMn_{1-x}Co_xO_3$. ΔM increases with increasing x. ΔM of $TmMn_{0.9}Co_{0.1}O_3$ starts at about 170 K, increases rapidly at about 50 K with decreasing temperature and exhibits a peak at around 20 K. A similar behavior can be seen for $TmMn_{0.7}Co_{0.3}O_3$, in which hexagonal and orthorhombic phases coexsist. ΔM of $TmMn_{0.5}Co_{0.5}O_3$, which is a nearly single orthorhombic phase, increases rapidly at about 60 K and exhibits a peak at around 22 K. The temperature at which ΔM has a maximum shifts slightly to higher temperature with increasing x. ΔM indicates the existence of a competition between ferromagnetic and antiferromagnetic interactions such as in a spin glass. Peña et al. reported the magnetic properties of orthorhombic $ErMe_xMn_{1-x}O_3$ (Me=Ni, Co) [7] and observed ZFC/FC variations in $ErNi_{0.33}Mn_{0.67}O_3$ similar to our results in $TmMn_{1-x}Co_xO_3$ between $x = 0.1$ and 0.5. They explained that this magnetization behavior of $ErNi_{0.33}Mn_{0.67}O_3$ was due to a competition between the antiferromagnetic inter-plane and the ferromagnetic in-plane interactions. A similar competing interaction is thought to exist also in the $TmMn_{1-x}Co_xO_3$ system, and the shift in the maximum temperature of ΔM is thought to be related to a change in the degree of the competition caused by a change in the composition, x, of Co.

Figure 4 shows the initial isothermal magnetizations of $TmMn_{0.6}Co_{0.4}O_3$ at several temperatures. The $M - H$ curves at 100 and 200 K are linear and paramagnetic. $TmMn_{0.6}Co_{0.4}O_3$ is ferromagnetic at 20 and 40 K, but the magnetization is not yet saturated in a field of 70 kOe. The ferromagnetic order is more stable at 20 K because spontaneous magnetization is observed at this temperature. However, a jump in the magnetization at 10 K is observed at around 10 kOe; the $M - H$ curve at 10 K is metamagnetic-like. These magnetization behaviors suggest that competing exchange interactions occur in a "ferromagnetic" state of $TmMn_{1-x}Co_xO_3$. Further investigations are required to clarify such complex magnetic behaviors. The interactions among mixed-valence cobalt and manganese ions and thulium ion that Peña et al. pointed out [7] are thought to be related, although the origin

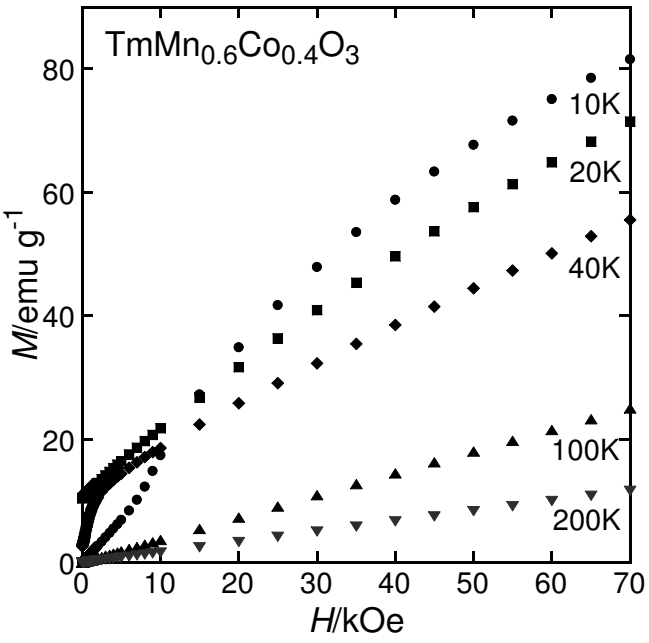

FIG. 4: Isothermal magnetization curves of $TmMn_{0.6}Co_{0.4}O_3$ at several temperatures.

of a metamagnetic-like jump is not clear yet.

III. CONCLUSIONS

Manganese perovskites $Tm_{1-y}Y_yMn_{1-x}Co_xO_3$ were prepared by a conventional solid-state reaction with Tm_2O_3, Mn_2O_3 and Co_3O_4. A pure phase of hexagonal $Tm_{1-y}Y_yMnO_3$ was obtained for $y \leqq 0.3$, and a single orthorhombic $TmMn_{1-x}Co_xO_3$ was synthesized for $x = 0.4$ and 0.5, except for a small amount of Tm_2O_3 impurity. $TmMn_{1-x}Co_xO_3$, in which Co is substituted for Mn, seems to have a ferromagnetic order at around 60 K. Competing exchange interactions are thought to produce a "ferromagnetic" state of this material.

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