Structure-related transport properties of A-site ordered perovskite
\[ \text{Sr}_3\text{ErMn}_{4-x}\text{Ga}_x\text{O}_{10.5-d} \]

W. Kobayashi†
Waseda Institute for Advanced Study, Waseda University, Tokyo 169-8050, Japan

T. Ishibashi
Department of Physics, Waseda University, Tokyo 169-8555, Japan
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We report x-ray diffraction, resistivity, thermopower, and magnetization of \[ \text{Sr}_3\text{ErMn}_{4-x}\text{Ga}_x\text{O}_{10.5-d} \], in which A-site ordered tetragonal phase appears above \( x = 1 \), and reveal that the system exhibits typical properties seen in the antiferromagnetic insulator with \( \text{Mn}^{3+} \). We succeed in preparing both A-site ordered and disordered phases for \( x = 1 \) in different preparation conditions, and observe a significant decrease of the resistivity in the disordered phase. We discuss possible origins of the decrease focusing on the dimensionality and the disordered effect.

I. INTRODUCTION

Perovskite oxide is denoted as \( \text{ABO}_3 \), where \( A \) and \( B \) represent lanthanide (and/or alkaline earth elements) and transition-metal elements, respectively. \( B \) ion is surrounded by six oxygen ions, and \( \text{BO}_6 \) octahedron is formed. The octahedron mainly contributes electrical and magnetic properties of the perovskite oxide. According to the ionic radius of \( A \) ion, the bond angle \( \angle B-O-B \) deviates from 180°, which causes a change of the bandwidth. In a substituted system of \( R^{3+}_{1-x}A^{2+}B\text{O}_3 \), the carrier concentration is also controlled as well as the bandwidth.

The A-site ordered manganese oxide \( \text{RBaMn}_2\text{O}_6 \) (\( R: \) lanthanide) has attracted much attention because of significant physical phenomena such as the large magnetoresistance of 1,000 % at room temperature \( [2] \), charge and orbital orderings at high temperatures \( [3] \). These properties attribute to A-site ordering working as “a periodic” Coulomb potential which stabilizes charge, spin, and/or intermediate-spin states of Co \( 3^+ \) ions and Ga \( 3^+ \) ions intermixed and/or orbital orderings at high temperatures \( [4] \). Owing to the randomness, A-site disordered phase of \( \text{R}_{0.5}\text{Ba}_{0.5}\text{Mn}_2\text{O}_3 \) displays the spin-glass state or the itinerant ferromagnetic state instead of the charge ordered state seen in the ordered phase \( [2, 5] \).

The A-site ordered cobalt oxide \( \text{Sr}_3\text{YC}_{0.4}\text{O}_{10.5} \) also exhibits peculiar magnetic properties with a high ferromagnetic (ferromagnetic) transition temperature of 335 K \( [6] \), which is in contrast with a spin state crossover near 100 K in \( \text{LaCoO}_3 \) \( [8] \). In this compound, the A-site ordering stabilizes oxygen deficient ordering, which makes a volume of the Co \( 6 \) octahedron larger than that of \( \text{LaCoO}_3 \) \( [8] \) and gives a different coordination number of Co \( 3^+ \) from \( \text{LaCoO}_3 \). These modifications stabilize high-spin and/or intermediate-spin states of Co \( 3^+ \) even at low temperatures, which causes the peculiar magnetic properties. Hence, partial substitution for the A-site or B-site cations strongly affects the spin state leading to significant suppression of the magnetic order; Ca substitution for Sr site \( [9] \) and 6%-Mn doping in the B site \( [10] \) destroys the room-temperature ferromagnetism of \( \text{Sr}_3\text{YC}_{0.4}\text{O}_{10.5} \).

Recently, a new A-site ordered perovskite \( \text{Y}_{0.8}\text{Sr}_{2.2}\text{Mn}_2\text{Ga}_0.79\text{O}_{10.5} \) (\( \text{Sr}_{2.93}\text{Y}_{1.07}\text{Mn}_{2.66}\text{Ga}_{1.34}\text{O}_{10.53} \)) was reported by Gillie \textit{et al.} \( [11] \), which is isostuctural to \( \text{Sr}_3\text{YCo}_{4}\text{O}_{10.5} \) \( [12, 13] \). As shown in Fig. 1, this compound has an octahedral site where \( \text{Mn}^{3+} \) ions mainly occupy with about 10%-Ga ions intermixed and a tetrahedral site where both \( \text{Mn}^{3+} \) and \( \text{Ga}^{3+} \) ions occupy. They found an antiferromagnetic state below 100 K in this material showing that \( \text{Y}_{0.8}\text{Sr}_{2.2}\text{Mn}_2\text{Ga}_0.79 \) was a antiferromagnetic insulator, however, they did not report the transport properties. We have prepared polycrystalline samples of \( \text{Sr}_3\text{ErMn}_{4-x}\text{Ga}_x\text{O}_{10.5-d} \) (\( x = 0, 0.5, 1, 2 \)) where \( d \) represents oxygen deficiency and investigated the transport and magnetic properties in relation to the structure. We have succeeded in preparing both A-site ordered and disordered phases for \( x = 1 \) using different preparation conditions and observe a significant decrease of the resistivity in the disordered phase. We attribute this to a change of dimensionality in conduction and/or A-site disordered effect. This material can be a good playground to study order-disorder effect on the electronic states of the antiferromagnetic insulator with \( \text{Mn}^{3+} \).
II. EXPERIMENTS

Polycrystalline samples of Sr$_3$ErMn$_{4-x}$Ga$_x$O$_{10.5-d}$ ($x = 0, 0.5, 1, 2$) were prepared by a solid state reaction. Stoichiometric amounts of SrCO$_3$, Er$_2$O$_3$, Mn$_3$O$_4$, and Ga$_2$O$_3$ were mixed, and the mixture was sintered at 1250 °C for 12 h for $x = 0$ and 0.5, 6 h for $x = 1$ and 2 in N$_2$ flow (100 – 200 ml/min). Then, the product was finely ground, pressed into a pellet, and sintered at 1250 °C for 12 h for $x = 0$, 24 h for $x = 0.5$, and 10 h for $x = 1$ and 2 in N$_2$ flow (100 – 200 ml/min). The second process was repeated 2 times for $x = 0.5$, and once for $x = 1$ and 2 with intermediate grindings and pelletizings. As shown in Fig. 2(c), $x = 1$ sample exhibits A-site ordered structure. We sintered the $x = 1$ sample again using the second process, and found the sample shows a disordered structure shown in Fig. 3.

The x-ray diffraction of the sample was measured using a standard diffractometer with Cu K$_{\alpha}$ radiation as an x-ray source in the $\theta - 2\theta$ scan mode. The structural simulations were performed using a RIETAN-2000 program [14]. The resistivity was measured by a four-probe method in a liquid He cryostat. The thermopower was measured using a steady-state technique in a liquid He cryostat with copper-constantan thermocouple to detect a small temperature gradient of about 1 K/cm. The magnetization was measured from 5 to 400 K by a commercial superconducting quantum interference device (SQUID, Quantum Design MPMS).

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction patterns of Sr$_3$ErMn$_{4-x}$Ga$_x$O$_{10.5-d}$ ($x = 0, 0.5, 1,2$). All the peaks are indexed as a cubic cell of the space group $Pm3m$ with the lattice parameter of $a \sim 3.8$ and 3.85 Å for $x = 0$ and 0.5, respectively. This cubic cell is also seen in Sr$_{1-x}$Y$_x$CoO$_{3-\delta}$ with small $x$ [8]. With increasing Ga content $x$, crystal structure changes from the cubic perovskite to a tetragonal A-site ordered perovskite (space group: $I4/mmm$, Fig. 1) with the lattice parameter of $a \sim 7.63$ and 7.65 Å, and $c \sim 15.58$ and 15.56 Å for $x = 1$ and 2, respectively. This result is consistent with the structural analysis by Gillie et al. [11]. As shown in the inset of Fig. 2(d), superstructure peaks corresponding to the A-site ordering are observed, while they do not appear for $x = 0$ and 0.5 samples. Ga ions selectively occupy the tetrahedral site to stabilize the A-site ordered structure as shown in Fig. 1 [11]. Thus, $x = 1$ is a minimal amount to stabilize the structure. Gillie et al. reported that the oxygen content of Sr$_2$YMn$_2$GaO$_{7.9}$ is 7.9 showing formal valence of Mn ion is almost 3+. Thus, it is assumed that the formal valence of Mn ion is also 3+ in the ordered compounds presented here.

Figure 3 shows the x-ray diffraction patterns of Sr$_3$ErMn$_{4-x}$Ga$_x$O$_{10.5-d}$ with different preparation conditions. Obviously, two patterns are different; one sample was identified to the tetragonal ordered phase (hereafter this is denoted by O sample), and the other was identified to the disordered-cubic perovskite phase (D sample). Similar structures are originally found in R$\text{BaMn}_2$O$_6$/R$\text{BaO}_{0.5}\text{MnO}_3$ systems [3]. We would like to say that the O sample is metastable so that the longer sintering stabilizes the disordered phase. Thus, this composition is just on the verge of order and disorder. As shown in the inset of Fig. 3, the superstructure peaks of D sample are hardly visible.

Figure 4 (a) shows the thermopower of Sr$_3$ErMn$_{4-x}$Ga$_x$O$_{10.5-d}$ ($x = 0, 0.5, 1, 2$). The magnitude of the thermopower is between 60 and 110
\( \mu \text{V/K} \), and the sign is negative showing that the carriers are electrons. Assuming that the formal Mn valence is 3+, we expect that a tiny amount of electrons on Mn\(^{2+}\) moves in the background of Mn\(^{3+}\) as shown in the inset of Fig. 4(a). Using an extended Heikes formula \( 15 \), the valence of Mn ion was evaluated to be 2.71+ at 300 K corresponding to \( d = 0.43 \) for \( x = 1 \) sample with spin degeneracy term of \( g_{\text{Mn}^{2+}} = 6 \) and \( g_{\text{Mn}^{3+}} = 5 \).

Figure 4 (b) shows the resistivity of \( \text{SrErMn}_{4-x}\text{Ga}_{x}\text{O}_{10.5-d} \) \( (x = 0, 0.5, 1, \text{ and } 2) \). Conducting temperature dependence is observed for all the samples. With \( x \), the magnitude of the resistivity decreases mainly due to decrease of scattering centers of the Ga ions. As seen in the inset of Fig. 4(b), the temperature dependence is described by an activation-type conduction \( \rho = \rho_0 \exp(\frac{E_g}{k_B T}) \) where \( E_g \) represents activation energy above 200 K. The activation energy \( E_g \) was evaluated to be 0.133, 0.146, 0.149, and 0.246 eV for \( x = 0, 0.5, 1, \text{ and } 2 \), respectively.

Figure 5(a) shows the magnetization of \( \text{SrErMn}_{4-x}\text{Ga}_{x}\text{O}_{10.5-d} \) \( (x = 0, 0.5, 1, \text{ and } 2) \). As shown in Figs. 5(b) and (c), the data was fitted by the Curie-Weiss law described by \( \chi = \frac{C}{T} + \chi_0 \), where \( C \), \( \theta_\text{W} \), and \( \chi_0 \) represent Curie constant, Weiss temperature and temperature independent term of the magnetic susceptibility, respectively. \( C \) was evaluated to be 0.023, 0.019, 0.026, and 0.018 emu/K g for \( x = 0, 0.5, 1, \text{ and } 2 \), corresponding to 12.34, 11.14, 13.17, and 11.07 \( \mu_B/\text{f.u.} \), respectively. These values are roughly explained by coexistence of 9.6 \( \mu_B \) of Er\(^{3+}\) with \( g = \frac{5}{2} \) and \( J = \frac{5}{2} \) and 3.87 \( \mu_B \) and 4.90 \( \mu_B \) in the high-spin states of Mn\(^{4+}\) and Mn\(^{3+}\). \( \chi_0 \) was evaluated to be \( 1.39 \times 10^{-5} \), \( 1.57 \times 10^{-5} \), 0, and 0 emu/g for \( x = 0, 0.5, 1, \text{ and } 2 \) samples, respectively. Since \( x = 0 \) and 0.5 samples show relatively good electric conductance compared with those of \( x = 1 \) and 2 samples, this contribution may come from conducting electrons. All the samples exhibit negative \( \theta_\text{W} \) \( (-45, -29, -52, \text{ and } -30 \text{ K for } x = 0, 0.5, 1, \text{ and } 2, \text{ respectively}) \) implying antiferromagnetic interaction in this system. At around 60 K, the slope of \( \chi^{-1} \) changes showing an existence of magnetic anomaly for all the samples. Since the antiferromagnetism was observed in \( \text{SrYMn}_2\text{GaO}_{8-d} \) below 100 K \( 11 \), the anomaly at around 60 K in \( \text{SrErMn}_{4-x}\text{Ga}_{x}\text{O}_{10.5-d} \) can be also related to antiferromagnetic order of Mn\(^{3+}\).

Lastly, we will discuss a difference of the transport and magnetic properties between the ordered (O sample) and disordered samples (D sample). Figure 6 (a) shows the temperature dependences of the resistivity of the O and D samples. The magnitude of the resistivity of the D sample is one order of magnitude smaller than that of the O sample, while the thermopower and magnetization of the D sample quite resemble those of the O sample as seen in Fig. 6(b). This strongly contrasts with the difference between the ferromagnetic-metal state of the disordered \( \text{R}_{0.5}\text{Ba}_{0.5}\text{MnO}_3 \) and charge-ordered insulating state of the ordered \( \text{RBA}_2\text{MnO}_5 \) \( 2 \). This variety of the properties comes from Mn\(^{3.5+}\) with the charge degree of freedom, while \( \text{SrErMn}_{4-x}\text{Ga}_{x}\text{O}_{10.5-d} \) has Mn\(^{3+}\) without the charge degree of freedom causing the small difference between the properties.

The difference of the resistivity shown in Fig. 6(a) is explained by several possible origins as follows: (1) a decrease of the carrier concentration, (2) an increase of the scattering time, (3) a change of dimensionality in con-
In summary, we have measured x-ray diffraction, resistivity, thermopower, and magnetization of \( \text{Sr}_3\text{ErMn}_4-x\text{Ga}_x\text{O}_{10.5-d} \) system, in which A-site ordered tetragonal phase appears above \( x = 1 \), and observed large negative thermopower, semiconducting conduction, and magnetic susceptibility with a kink at 60 K implying antiferromagnetism. We succeed to prepare both A-site ordered and disordered phases for \( x = 1 \) sample and observe a significant decrease of the resistivity in the disordered phase. We attribute this to a change of dimensionality in conduction and/or a change of electronic structure induced by the disordering of A sites.

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[1] email address: kobayashi-wataru@suou.waseda.jp
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