Comparative study of ordered and disordered $Y_{1-x}Sr_xCoO_3-\delta$

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We have succeeded in preparing $A$-site ordered- and disordered-$Y_{1/4}Sr_{3/4}CoO_3-\delta$ with various oxygen deficiencies $\delta$, and have made comparative study of their structural and physical properties. In the $A$-site ordered structure, oxygen vacancies order, and $\delta = 0.34$ sample shows a weak ferromagnetic transition beyond 300 K. On the other hand, in the $A$-site disordered structure, no oxygen vacancy ordering is observed, and $\delta = 0.16$ sample shows a ferromagnetic metallic transition around 150 K. $A$-site disordering destroys the orderings of oxygen-vacancies and orbitals, leading to the strong modification of the electronic phases.

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Cobalt oxides with perovskite-based structure exhibit many attracting phenomena such as ferromagnetism, metal-insulator transition, and spin-state transition. These phenomena are caused by the various spin states of Co ion such as low-spin (LS), intermediate-spin (IS), and high-spin (HS) states. $La_{1-x}Sr_xCoO_3$ is the most typical example: The ground state of $x = 0$ compound is a nonmagnetic insulator with LS state of Co$^{3+}$.

With increase of Sr content $x$, a ferromagnetic metallic state emerges in $x \geq 0.18$, which is driven by the double-exchange interaction between Co$^{3+}$ in LS state and Co$^{3+}$ in IS state.

Among many perovskite cobaltites, $Y_{1-x}Sr_xCoO_3-\delta$ attracts our interest, because of its characteristic structural features and high magnetic-transition temperatures. $A$-site ordered-$Y_{1-x}Sr_xCoO_3-\delta$ has been first reported by Withers et al. and Istomin et al. This compound has large oxygen deficiency $\delta$. The structure of ordered-$Y_{1/4}Sr_{3/4}CoO_2.66$ can be regarded as the alternate stacking of AO and Co$_{1.7}$ sheets, where $A$-site cations and oxygen vacancies concomitantly order as shown in Fig. 1(a). $Y_{1/4}Sr_{3/4}O$ sheet stacks along the $c$-axis with translation $(1/2, 1/2, 0)$. Co$_{0.3}$ and Co$_{0.2}$ sheets alternately stack along the $c$-axis with translation $(1/2, 1/2, 0)$ to form the four times periodicity. For $0.75 \leq x \leq 0.8$, $A$-site ordered-$Y_{1-x}Sr_xCoO_3-\delta$ undergoes a weak ferromagnetic transition at 335 K. Ishiwata et al. propose that the weak ferromagnetism is related to the orbital ordering. In addition, the physical properties are sensitive to the variation of oxygen deficiency $\delta$. For example, in $x = 0.33$, the ground state is transformed from an antiferromagnetic insulator to a ferromagnetic metal with a slight decrease of $\delta$.

The high magnetic transition temperature is due to the $A$-site ordered structure free from chemical disorder. The $A$-site arrangement in perovskite-based oxides plays an important role in determining their physical properties. In $A$-site ordered-$R_1/2Ba_{1/2}MnO_3$ ($R$ = rare earth ion), ferromagnetic or charge-ordering transitions exceed room temperature, and a bicuspid feature can be seen in the phase diagram. The random potential arising from $A$-site disordering suppresses long-range orders, and gives rise to the colossal magnetoresistive state near the bicritical region. In the cobalt oxide system just like the manganese oxide system, the $A$-site arrangement probably affects the physical properties through Co spin state and orbital arrangement. However, there are few reports on randomness effect of $A$-site ions in the cobalt oxides.

In this study, we prepared $A$-site ordered- and disordered-$Y_{1/4}Sr_{3/4}CoO_3-\delta$ with various $\delta$ and have made a comparative study of them in order to investigate the $A$-site randomness effect on their structural and physical properties.

$A$-site ordered- and disordered-$Y_{1/4}Sr_{3/4}CoO_3-\delta$ were prepared in a polycrystalline form by solid state reaction. Mixed powders of $Y_2O_3$, SrCO$_3$, and CoO were mixed...
heated at 1073 K in air with a few intermediate grindings, and sintered at 1423 K in air. Then the sample was annealed at 1173 K in Ar atmosphere. The resulting product has A-site ordered form. On the other hand, A-site disordered form is obtained by quenching the sample from 1473 to 77 K. We prepared ordered and disordered-$Y_{1/4}Sr_{3/4}CoO_3$ with various $\delta$ through different annealing conditions. The detailed conditions will be described elsewhere. The values of $\delta$ were determined through iodometric titration with an accuracy of $\pm$ 0.01. The crystallographic analysis of the obtained samples was performed by X-ray-diffraction (XRD) method at room temperature. The resistivity was measured by a standard four-probe method from 5 to 350 K. The magnetic properties were measured using a Quantum Design, Physical Property Measurement System (PPMS) from 5 to 350 K.

From the XRD measurements, we confirmed that $Y_{1/4}Sr_{3/4}CoO_3$ annealed in Ar has the A-site ordered structure as shown in Fig. 1(a). A-site ordered-$Y_{1/4}Sr_{3/4}CoO_3$ with $\delta = 0.44$ and 0.30 have the similar A-site ordered structure as that of $\delta = 0.34$ sample, but the arrangement of oxygen vacancies are different from each other. On the other hand, quenched $Y_{1/4}Sr_{3/4}CoO_3$ ($0.15 \leq \delta \leq 0.27$) samples have a simple cubic perovskite structure. Bragg peaks arising from A-site and/or oxygen-vacancy orderings are not observed, indicating that $Y^{3+}$ and Sr$^{2+}$ randomly occupy A-site, and that oxygen vacancies are randomly distributed as shown in Fig. 1(b). These results indicate that A-site disordering makes the oxygen-vacancy order destabilized. The detailed results of the structural properties will be published elsewhere.

Figure 2(a) shows the temperature dependence of the magnetization ($M$-$T$) of A-site ordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$. The magnetization of $\delta = 0.34$ shows an abrupt increase below 330 K. The onset of the magnetization corresponds to the weak ferromagnetic transition. The magnetic field dependence of the magnetization ($M$-$H$) shows a ferromagnetic behavior at 300 K, but the magnetization remains unsaturated even at 80 kOe ($M = 0.19 \mu_B$/Co). This magnetic behavior is consistent with that reported by Kobayashi et al. On the basis of structural refinement, they propose two models for the magnetic order. One is a canted antiferromagnetic state, and the other is a ferrimagnetic state due to the antiferromagnetic coupling between the HS and IS states of Co$^{3+}$. Slight increase or decrease of $\delta$ from 0.34 suppresses the weak ferromagnetic phase around 325 K. The magnetization of $\delta = 0.30$ gradually increases below 250 K, and shows weak ferromagnetic behavior at low temperatures. On the other hand, $\delta = 0.44$ shows a magnetic transition around 230 K. The magnetization of $\delta = 0.44$ sample linearly depends on applied magnetic fields at 5 K, while the $M$-$H$ curves of $\delta = 0.34$ and 0.30 indicate that they have ferromagnetic components. With decrease of $\delta$ from 0.44, that is, with increase of Co valence, the ferromagnetic component tends to increase at low temperatures. The magnetization of $\delta = 0.44$, 0.34, and 0.30 at 80 kOe are 0.127, 0.132, and 0.23 $\mu_B$/Co, respectively.

Figure 2(b) shows the $M$-$T$ curves of A-site disordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$. The magnetization of $\delta = 0.15$ exhibits an abrupt jump around 150 K. The $M$-$H$ curve of $\delta = 0.15$ shows the typical ferromagnetic hysteresis below 150 K, in contrast to that of ordered-$Y_{1/4}Sr_{3/4}CoO_2$.66. The saturation magnetization of $\delta = 0.15$ at 5 K is 1.2 $\mu_B$/Co. With increase of $\delta$, the ferromagnetic phase is drastically suppressed. The magnetic transition temperatures of A-site disordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$ are much lower than those of A-site ordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$. As shown in the inset of Fig. 2(b), the temperature dependence of inverse susceptibility ($H/M$-$T$) of disordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$ ($\delta = 0.15$, 0.16, and 0.22) obeys Curie-Weiss law above 250 K with Weiss temperatures $\theta = 190.3$, 169.1, and 134.1 K, and effective moments estimated from the observed slopes in this region are $P_{eff} = 3.06$, 3.02, and 3.00 $\mu_B$/Co, respectively. This result indicates that magnetic interaction among Co-spins is ferromagnetic for disordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$ with $\delta = 0.15$ to 0.22.

Figure 3(a) shows the temperature dependence of the resistivity ($\rho$-$T$) of A-site ordered-$Y_{1/4}Sr_{3/4}CoO_3$-$\delta$. The resistivities of all the samples show semiconducting or insulating behavior. With decrease of $\delta$, the resistivity abruptly drops over the whole temperatures. Taking into account the results of the $M$-$T$ curves, this implies...
the increase of ferromagnetic metallic components except for \( \delta = 0.34 \) having large ferromagnetic component. \( \delta = 0.34 \) shows a clear kink around 300 K, which corresponds to the enhanced weak ferromagnetic transition. Figure 3(b) shows the \( \rho - T \) curves of A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\). \( \delta = 0.27 \) shows insulating behavior. With decrease of \( \delta \), the resistivity is steeply decreased similar to the case of A-site ordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\), and \( \delta = 0.15 \) sample shows almost metallic behavior.

Then, we will discuss the effect of A-site disordering on the structural properties of Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\). In the A-site ordered structure (0.30 \( \leq \delta \leq 0.44 \)), the periodic-potential and lattice-distortion associated with Y/Sr ordering are likely to stabilize the oxygen-vacancy order and orbital order. In contrast, in A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) (0.15 \( \leq \delta \leq 0.27 \)), the random-potential and lattice-distortion due to Y/Sr disordering destroy the oxygen-vacancy order.

Such randomness strongly affects the physical properties as well as the structural properties. As shown in Fig. 2, the magnetic transition temperatures of A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) are much lower than those of ordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\). Furthermore, a deviation of \( \delta \) from 0.34 as well as A-site disordering has much effect on the magnetic structure. In A-site ordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\), \( \delta = 0.34 \) shows the highest magnetic transition temperature (the weak ferromagnetic transition at 330 K). As described above, the oxygen-vacancy ordered structure depends on \( \delta \). The oxygen-vacancy ordering pattern near \( \delta = 0.34 \) may be essential for the weak ferromagnetism. The relation between the arrangement of oxygen-vacancy and the magnetic structure is now under investigation. The magnetic and transport properties of A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) resemble those of La\(_{1-x}\)Sr\(_x\)CoO\(_3\). In La\(_{1-x}\)Sr\(_x\)CoO\(_3\), the magnetization and the magnetic transition temperature increase continuously with increasing Sr content \( x \) or Co valence, and the ferromagnetic metallic state is dominant for \( x \geq 0.18 \). The ferromagnetic metallic state of A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) is likely to be attributed to double-exchange interaction just like the case of La\(_{1-x}\)Sr\(_x\)CoO\(_3\).

In summary, we have prepared A-site ordered- and disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\), and have investigated their structural and physical properties. Oxygen vacancy orders in the A-site ordered structure, but not in the A-site disordered structure. A-site disordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) exhibits the magnetic transition below 150 K, which is quite lower than those of ordered-Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\). The A-site randomness suppresses magnetic order in cobalt oxide Y\(_{1/4}\)Sr\(_{3/4}\)CoO\(_3\)\(\delta\) as reported in manganese oxide R\(_{2/3}\)Ba\(_{1/3}\)MnO\(_3\).

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