Co-Substitution Effect in Room-Temperature Ferromagnetic Oxide Sr₃.₁Y₀.₉Co₄O₁₀.₅

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Abstract: We investigated the Co substitution effect for the magnetic properties in room-temperature ferromagnetic oxide Sr₃.₁Y₀.₉Co₄O₁₀.₅. The substituted element (Al and Ga) and low-spin state Co³⁺, which was changed from a high-spin or intermediate-spin state by Al or Ga substitution, reduced the Curie temperature to even 1.5 times lower than the temperature estimated from a simple dilution effect. Al³⁺ preferentially substituted for intermediate-spin-state Co³⁺ in the ferrimagnetic CoO₆ layer and deteriorated the saturation magnetization of Sr₃.₁Y₀.₉Co₄O₁₀.₅. By contrast, Ga³⁺ substituted for high-spin-state Co³⁺ in the CoO₆ layer and/or the antiferromagnetic CoO₄.₅ layer and enhanced the saturation magnetization per Co ion. These results indicate that the magnetic properties of Sr₃.₁Y₀.₉Co₄O₁₀.₅ can be controlled by selectively substituting for Co³⁺ with different spin states.

Keywords: cobalt oxide; elemental substitution; room temperature ferromagnetism; spin state

1. Introduction

Among transition metal oxides with various functions, cobalt oxides are especially interesting compounds and attract attention from many researchers. Layered cobalt oxides (Na₀.₅CoO₂ and Ca₃Co₄O₇) with unusual thermoelectric properties [1–4], REBa₂Co₅.₃ (RE = rare earth) with giant magnetoresistance [5–7], and LaCoO₃ with temperature-induced spin-state transitions [8–13] are typical compounds that have been actively studied. Co³⁺ ions take three types of spin state: the low-spin (LS; S = 0) state of (t₂g)⁶ and the high-spin (HS; S = 2) state of (e_g²(t₂g)⁴, as well as the intermediate-spin (IS; S = 1) state of (e_g)¹(t₂g)⁵. The spin state of Co³⁺ ions is strongly related to the functions and phenomena of the cobalt oxides, and unraveling the origins of these functions has opened up new material design guidelines.

The A-site-ordered perovskite Sr₃.₁Y₀.₉Co₄O₁₀.₅ is a weak-ferromagnetic (ferrimagnetic) material at room temperature. The transition temperature (Tc: Curie temperature) has been reported to be around 340 K for polycrystalline samples [14] and 370 K for single-crystalline samples [15]. The crystal structure of Sr₃.₁Y₀.₉Co₄O₁₀.₅ is shown in Figure 1a. The octahedral CoO₆ layer and the oxygen-deficient (tetrhedral/pyramidal) CoO₄.₅ layer, which consists of tetrhedral CoO₄ and pyramidal CoO₃, are stacked alternately [16–19]. In this system, the two structural-phase transitions have been revealed in Sr₃.₁₂Er₀.₈₈Co₄O₁₀.₅ [20,21]. The space group of tetragonal I₄/mmm in the highest-temperature phase with a 2a × 2a × 4a unit cell, where a is the lattice parameter of the primitive perovskite unit cell, changes into monoclinic A2/m with a 2√2a × 2√2a × 4a supercell due to oxygen vacancy ordering at 509 K. Further, the lowest-temperature phase, in which the a-axis is doubled (4√2a
\(x \times 2\sqrt{2a} \times 4a\), appears due to a spin state and/or orbital ordering at 360 K. The origin of ferromagnetism in \(\text{Sr}_{3.1}\text{Y}_{0.9}\text{CoO}_{4.0.5}\) has been revealed as the ferrimagnetism of the CoO\(_6\) layer \([14,20,22]\). In the CoO\(_6\) layer, both HS- and IS-state Co\(^{3+}\) exist, where the majority component is the IS state \([23]\). All the Co\(^{3+}\) ions in the CoO\(_{4.25}\) layer take the HS state and align antiparallel to show antiferromagnetic order \([21]\). Figure 1b shows the magnetic structure of \(\text{Sr}_{3.1}\text{Y}_{0.9}\text{CoO}_{4.0.5}\). The saturation magnetization simply expected from this structure is 0.25 \(\mu_B/\text{Co}\). In this material, a spin-state crossover, which is a change from the HS- and IS-states in the CoO\(_6\) layer into the LS state, is observed around 150 K. Additionally, it has been reported that the spin-state crossover is enhanced by physical pressure \([24]\) and chemical pressure owing to the pressure-induced enlargement of the crystal-field splitting \([25]\).

In this interesting cobalt oxide, so far, various kinds of investigations \([26-30]\) have been conducted and the A-site substitution has been actively studied in order to reveal and control the spin state of Co ions \([25,31,32]\).

![Crystal Structure and Magnetic Structure of Sr\(_{3.1}\text{Y}_{0.9}\text{CoO}_{4.0.5}\)](image)

*Figure 1. (a) Crystal structure and (b) magnetic structure of Sr\(_{3.1}\text{Y}_{0.9}\text{CoO}_{4.0.5}\).*

In this study, we substituted nonmagnetic elements of Al and Ga with different ionic radii for the B-site (Co-site) and measured the magnetic properties of \(\text{Sr}_{3.1}\text{Y}_{0.9}\text{Co}_{4-x}\text{B}_x\text{O}_{10.5}\) \((B = \text{Al and Ga}; x = 0, 0.2, \text{and } 0.4)\). It was expected that the Curie temperature would be reduced towards room temperature by a simple dilution effect. Moreover, the ferrimagnetism of the CoO\(_6\) layer, which is responsible for the magnetization of \(\text{Sr}_{3.1}\text{Y}_{0.9}\text{CoO}_{4.0.5}\), was expected to be controlled through selective substitution.

2. Experimental

\(\text{Sr}_{3.1}\text{Y}_{0.9}\text{Co}_{4-x}\text{B}_x\text{O}_{10.5}\) \((B = \text{Al and Ga}; x = 0, 0.2, \text{and } 0.4)\) polycrystalline samples were prepared by a solid-state reaction. SrCO\(_3\), Y\(_2\)O\(_3\), Co\(_3\)O\(_4\), Al\(_2\)O\(_3\), and Ga\(_2\)O\(_3\) were mixed and calcined at 1100 °C for 12 h in air. The calcined products were ground, pressed into pellets, and sintered at 1100 °C for 48 h in air. To compensate Co evaporation during calcining and sintering, 5-mol% Co\(_3\)O\(_4\) was added from the stoichiometric ratio, following the previous report \([25]\).

X-ray diffraction (XRD) patterns of the ground samples were taken with CuK\(_\alpha\) \((\lambda = 1.5418 \text{ Å})\) radiation using a standard diffractometer with monochromator (Rigaku, SmartLab, Tokyo, Japan). The 2θ scan was carried out with a continuous-scan mode from 20 to 80° at 5°/min. The magnetization was measured from 2 to 350 K by a commercial superconducting quantum interference device magnetometer (Quantum Design, MPMS, San Diego, CA, USA). We applied \(\mu_0H = 0.1 \text{ T}\) for the measurement of magnetization–temperature \((M–T)\) data and measured the magnetization \(M\) in sweeping field \(\mu_0H\) from \(-7\) to 7 T at 2 K.
3. Results and Discussion

Figure 2a shows the XRD patterns of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ powders. All the peaks of the samples are indexed as Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ phase without any impurity phases. The 2θ values systematically shift according to the substituted element and amount. The axis lengths and the lattice volumes calculated from the XRD patterns are shown in Figure 2b. Both $a$- and $c$-axis lengths of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Al$_x$O$_{10.5}$ are found to decrease with increasing Al content within experimental uncertainties. On the other hand, in Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Ga$_x$O$_{10.5}$, the two lengths increase with increasing Ga content. Consequently, the lattice volumes of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Al$_x$O$_{10.5}$ and Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Ga$_x$O$_{10.5}$ decrease and increase with increasing $B$ content, respectively. The ionic radii of Co$^{3+}$, Al$^{3+}$, and Ga$^{3+}$ are listed in Table 1. In the case of Co$^{3+}$, the radii depend on the spin state. Co$^{3+}$ ions in any spin state are larger than Al$^{3+}$ ions and smaller than Ga$^{3+}$ ions. The changes in lattice volume due to Co substitution are well explained in terms of the ionic radii, but the substitution sites for both Al$^{3+}$ and Ga$^{3+}$ could not be determined from the axis length and the lattice volume.

![Figure 2](image_url)

**Figure 2.** (a) XRD (CuKα) patterns of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ ($B =$ Al and Ga: $x = 0, 0.2, 0.4$) powders. (b) The axis lengths and the lattice volumes of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ as a function of $B$ content.

**Table 1.** Ionic radii of high-spin (HS), intermediate-spin (IS), and low-spin (LS) states Co$^{3+}$, Al$^{3+}$, and Ga$^{3+}$.

| Ion   | Co$^{3+}$(HS) [33] | Co$^{3+}$(IS) [34] | Co$^{3+}$(LS) [33] | Al$^{3+}$ [33] | Ga$^{3+}$ [33] |
|-------|--------------------|--------------------|--------------------|----------------|----------------|
| Radius [Å] | 0.61               | 0.56               | 0.545              | 0.535          | 0.62           |

Figure 3a shows the field-cooled M–T curves of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$. In both cases of $B = $ Al and Ga, the magnetic transition shifts to low temperatures with increasing substitution amounts of $B$. The Curie temperature ($T_c$) is unable to be determined using the Curie–Weiss law because the magnetic transition of this system is of first order. Then, we estimate the $T_c$ from inflection points in the temperature derivative of the M–T curves.

The normalized $T_c$ ($T_c(x)/T_c(0)$) of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ by $T_c$ of Sr$_{3.1}$Y$_{0.9}$Co$_{4}$O$_{10.5}$ is shown in Figure 3b as a function of substitution ratio of Co by $B$ ($x/4$). The expected $T_c$ reduction from a simple dilution effect due to Co substitution is shown by the dashed line. The $T_c$’s of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Al$_x$O$_{10.5}$ and Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Ga$_x$O$_{10.5}$ coincide with each other and are 1.5 times lower than the $T_c$ expected from the dilution effect. Assuming that the dilution effects is valid, we expect that the Al and Ga substitutions should generate additional nonmagnetic Co ions. In other words, Al or Ga substitution for the Co site

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![Figure 2](image_url)

**Figure 2.** (a) XRD (CuKα) patterns of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ ($B = $ Al and Ga: $x = 0, 0.2, 0.4$) powders. (b) The axis lengths and the lattice volumes of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ as a function of $B$ content.

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|-------|--------------------|--------------------|--------------------|----------------|----------------|
| Radius [Å] | 0.61               | 0.56               | 0.545              | 0.535          | 0.62           |

Figure 3a shows the field-cooled M–T curves of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$. In both cases of $B = $ Al and Ga, the magnetic transition shifts to low temperatures with increasing substitution amounts of $B$. The Curie temperature ($T_c$) is unable to be determined using the Curie–Weiss law because the magnetic transition of this system is of first order. Then, we estimate the $T_c$ from inflection points in the temperature derivative of the M–T curves.

The normalized $T_c$ ($T_c(x)/T_c(0)$) of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$B$_x$O$_{10.5}$ by $T_c$ of Sr$_{3.1}$Y$_{0.9}$Co$_{4}$O$_{10.5}$ is shown in Figure 3b as a function of substitution ratio of Co by $B$ ($x/4$). The expected $T_c$ reduction from a simple dilution effect due to Co substitution is shown by the dashed line. The $T_c$’s of Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Al$_x$O$_{10.5}$ and Sr$_{3.1}$Y$_{0.9}$Co$_{4-x}$Ga$_x$O$_{10.5}$ coincide with each other and are 1.5 times lower than the $T_c$ expected from the dilution effect. Assuming that the dilution effects is valid, we expect that the Al and Ga substitutions should generate additional nonmagnetic Co ions. In other words, Al or Ga substitution for the Co site...
may drive neighboring $\text{Co}^{3+}$ from the HS or IS state into the nonmagnetic LS state. The magnetization reduction due to the spin-state crossover, which is indicated by the thick arrow in Figure 3a, is observed around 150 K only in $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$. Hence, both Al and Ga substitutions suppress the spin-state crossover. The transition from the HS or IS state to the LS state at low temperature is no longer necessary because some $\text{Co}^{3+}$ has already been stabilized to the LS state by Al/Ga substitution.

The high-field magnetization depends on the substitution element and amount. Since the $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ system shows ferrimagnetic order, the magnetization does not saturate but continues to increase with the increasing magnetic field. Then, we define the saturation magnetization ($M_s$) as the $y$ intercept of the linearly extrapolated line from the high-field $M$–$H$ curve, as shown by the dashed line in Figure 4a.

The magnetic field dependence of magnetization of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ at 2 K is shown in Figure 4a. The high-field magnetization depends on the substitution element and amount. Since the $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ system shows ferrimagnetic order, the magnetization does not saturate but continues to increase with the increasing magnetic field. Then, we define the saturation magnetization ($M_s$) as the $y$ intercept of the linearly extrapolated line from the high-field $M$–$H$ curve, as shown by the dashed line in Figure 4a.

The $M_s$ of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ at 2 K is shown in Figure 4b as a function of the $B$ content $x$. The $M_s$ of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{O}_{10.5}$ is smaller than the $M_s = 0.25 \mu_B$/Co expected from the magnetic structure because some magnetic $\text{Co}^{3+}$ has experienced the spin-state crossover to the nonmagnetic LS state at 2 K. Since $M_s$ is referred to as the magnetization per Co ion (not per unit cell), $M_s$ is expected to remain intact if Al or Ga is substituted for Co randomly. If we ascribe the 1.5-times faster reduction of $T_c$ to nonmagnetic Co ions additionally induced by Al/Ga substitution, Al/Ga substitution drives some portions of the neighboring Co ions to the LS state. We can estimate an amount of LS-state Co ions induced by Al/Ga substitution by assuming that the dilution effect is valid. Taking the estimated amount of LS-state Co ions with Al/Ga random substitution into account, we evaluate $M_s$ to be 0.243 and 0.236 $\mu_B$/Co at $x = 0.2$ and 0.4, respectively, as shown by the open circles. The $M_s$ of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{Al}_2 \text{O}_{10.5}$ is smaller than the calculated values and decreases with increasing Al content. On the other hand, the $M_s$ of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{Al}_2 \text{O}_{10.5}$ is smaller than the calculated values and decreases with increasing Al content. These obvious differences between Al and Ga substitutions suggest different substitution sites.

![Figure 3](image-url)

**Figure 3.** (a) Temperature dependence of the magnetization of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ ($B = \text{Al}$ and $B = \text{Ga}$: $x = 0, 0.2,$ and 0.4) under 0.1 T. (b) The normalized Curie temperature ($T_c(x)/T_c(0)$) of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{B}_2 \text{O}_{10.5}$ by $T_c$ of $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_4 \text{O}_{10.5}$ as a function of substitution ratio of Co by $B$ ($x/4$). $T_c$ has been estimated from the inflection points in the temperature derivative of the $M$–$T$ curve.
The saturation magnetization of Sr\textsuperscript{3+} substitution is not made clear in this study but should be revealed in future work.

\[ M_s = \frac{2}{3} \mu_B \text{Co} \]

Finally, we estimate \( M_s \) of Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}B\textsubscript{x}O\textsubscript{10.5} along with our suggestion. It is assumed that the LS-state Co ions induced by Al/Ga substitution distribute randomly. If Ga substitutes for the HS-state Co\textsuperscript{3+} in the CoO\textsubscript{6} or CoO\textsubscript{4.25} layers randomly, \( M_s \)'s are estimated to be 0.271 and 0.292 \( \mu_B/\text{Co} \) at \( x = 0.2 \) and 0.4, respectively. Both values are in good agreement with the measured values shown in Figure 4b. On the other hand, if Al substitutes for the IS-state Co\textsuperscript{3+} in the CoO\textsubscript{6} layer, \( M_s \)'s are estimated to be 0.205 and 0.157 \( \mu_B/\text{Co} \) at \( x = 0.2 \) and 0.4, respectively. The values are somewhat smaller than the measured values. Therefore, Al mainly substitutes for the IS-state Co\textsuperscript{3+}, but a part of Al would also substitute HS-state Co\textsuperscript{3+}.

4. Conclusions

We measured and analyzed the magnetic properties of Co-substituted Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}B\textsubscript{x}O\textsubscript{10.5} (B = Al and Ga: \( x = 0, 0.2, \) and 0.4). We found that the Curie temperatures of both Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}Al\textsubscript{x}O\textsubscript{10.5} and Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}Ga\textsubscript{x}O\textsubscript{10.5} are about 1.5 times lower than the temperature estimated from the simple dilution effect. This extra Curie-temperature reduction is understood in terms of the LS-state Co\textsuperscript{3+} additionally induced by the Co site substitution. A mechanism of the LS-state Co\textsuperscript{3+} inducement by the substitution is not made clear in this study but should be revealed in future work. The saturation magnetization of Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}Al\textsubscript{x}O\textsubscript{10.5} decreases with Al content, whereas that of Sr\textsubscript{3.1}Y\textsubscript{0.9}Co\textsubscript{4−x}Ga\textsubscript{x}O\textsubscript{10.5} increases with Ga content. This different behavior suggests the selectivity

\[ B = \text{Al}, 2 \text{ K} \]

\[ B = \text{Ga}, 2 \text{ K} \]

\[ M_s = \frac{2}{3} \mu_B \text{Co} \]

\[ B = \text{Al} \]

\[ B = \text{Ga} \]

\[ \text{Estimated value} \]
of the substitution site depends on the substituted element. $\text{Al}^{3+}$ close to the IS-state $\text{Co}^{3+}$ in ionic size suppresses the magnetization through substituting the majority component of the IS-state $\text{Co}^{3+}$ in the ferrimagnetic $\text{CoO}_6$ layer. By contrast, the substitution for the minority component of the HS-state $\text{Co}^{3+}$ in $\text{CoO}_3$ layer and/or HS-state $\text{Co}^{3+}$ in antiferromagnetic $\text{CoO}_{1.25}$ layer by $\text{Ca}^{2+}$ enhances the magnetization. The present study suggests that the magnetization of the room-temperature ferromagnetic oxide $\text{Sr}_{3.1} \text{Y}_{0.9} \text{Co}_3 \text{O}_{10.5}$ can be controlled by the selective substitution for $\text{Co}$ site according to the ionic radius of the substituting elements.

**Author Contributions:** S.K., A.T., and I.T. conceived and designed the experiments; S.K. and A.T. performed the experiments; S.K. and I.T. analyzed the data; M.M., Y.K., Y.M., and A.F. helped with the experiments and discussed the results; A.T. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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