Effect of Y doping on the magnetic properties of the postlayered perovskite Sr$_3$Co$_2$O$_6$

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Abstract. Polycrystals of the postlayered perovskite Sr$_{3-x}$Y$_x$Co$_2$O$_6$ ($x=0-0.3$) are successfully synthesized under a high-pressure and high-temperature condition, followed by magnetic susceptibility and magnetization measurements. The magnetically ordered state of the host compound Sr$_3$Co$_2$O$_6$ is quickly altered by the Y doping. The characteristic magnetization plateaus is smeared out and disappears at $x = 0.3$. The magnetic properties change is much faster than what was observed for the Y doped analogous compound Ca$_3$Co$_2$O$_6$, reflecting a possible difference of degree of the magnetic anisotropy of the Co spins of the Ca and Sr compounds.

1. Introduction

A perovskite oxide heated under high-pressure and high-temperature conditions generally has a chance to crystalize in an isocompositional denser form such as the post-perovskite, which is often useful to investigate nature of the lower Earth’s mantle [1-8]. Besides, the denser form usually has a largely altered structure, thus rigorously different magnetic properties can be expected to appear. For example, the postperovskite CaRhO$_3$ and CaRuO$_3$ [1,6] show significantly different magnetic properties from those of the perovskite CaRhO$_3$ and CaRuO$_3$, indicating that the electronic ground state is indeed changed via the squeezing.
The postlayered perovskite Sr$_3$Co$_2$O$_6$ was recently synthesized by heating at 1400 °C and 6 GPa; the compound is ~6% denser than the regular form [9]. The compound is isostructural with the spin-chain compound Ca$_3$Co$_2$O$_6$, which crystallizes in a K$_4$CdCl$_6$-type rhombohedral structure with a space group of $R$-3c [10]. The structure consists of alternate stacking of the face-sharing CoO$_6$ octahedra (Co1) and the trigonal prisms (Co2) along the $c$-axis and Ca(Sr) spacers. Interestingly, both the Sr and Ca compounds show almost identical magnetic properties including multiple transitions to the ferromagnetic (FM) and partially disordered antiferromagnetic (AFM) states. A 1/3 magnetization plateaus is commonly observed for both the compounds. The complicated magnetic behaviors are generally referred to a geometrical frustration of spin-chains in a triangular lattice. The so-far studies suggest that both the compound may share the common physics of the possible triangular magnetism.

Some parts of the magnetic properties of Sr$_3$Co$_2$O$_6$, however, remains to be largely different from those of Ca$_3$Co$_2$O$_6$: the magnetic anisotropy between the inter-chain and the intra-chain of Ca$_3$Co$_2$O$_6$ is relatively high ($D$~ -25 K) [11]. The principal origin of the anisotropy is generally considered as the Ising-type Co spins, which may also be responsible for the cause of the 1/3 magnetization plateaus. However, Sr$_3$Co$_2$O$_6$ has been suggested to have a much smaller magnetically anisotropic energy in nature [9]. If this is true, the origin of the magnetic plateaus may need to be reconsidered. In this study, we investigated the effect of Y doping on the magnetic properties of the postlayered perovskite Sr$_3$Co$_2$O$_6$. The small amount of the doped Y is fond to largely change the magnetic states.

### 2. Experimental

Polycrystalline Sr$_{3-x}$Y$_x$Co$_2$O$_6$ ($x=0, 0.1, 0.2, 0.3$) were prepared from Co powder (99.5%), laboratory-made SrO$_2$, Y$_2$O$_3$ (99.9%), and KClO$_4$ (99.5%) in a belt-type high-pressure. The stoichiometric mixtures of those were heated in the press at 6 GPa and 1400 °C for 1 hr. Details of the synthesis are available elsewhere [9]. Phase purity of the high-pressure products was examined by powder X–ray diffraction (XRD) in Panalytical X’Pert Pro multipurpose X-ray diffractometer with CuKα radiation. The scanning 2θ range was from 10° to 70° with a step of 0.02°. Temperature dependence of dc magnetic susceptibility ($\chi$) was measured in a magnetic properties measurement system (Quantum Design) between 2 K and 300 K in a magnetic field of 5 kOe. Loose powder for each composition was used for the measurement. Isothermal magnetization was measured at 5 K in the magnetic field range of ± 50 kOe in the same apparatus.

### 3. Results and discussion

Figure 1 (a) shows the XRD patterns for all the samples. All major peaks are well characterized as was done for the host compound Sr$_3$Co$_2$O$_6$ [9], though trivial peaks for CoO are visible over the composition range. For further clarification, a horizontally expanded view is shown in Figure 1 (b); the major peak (113) slightly shifts toward the lower 2θ angle with increasing the Y content, while the peak (030) remains almost at the same position. To see more details, the lattice parameters for all the samples are calculated in the analysis of the XRD patterns and the results are summarized in Table 1. It appears that the lattice change by the Y doping is apparently anisotropic: $c$ increases monotonically from 10.701 Å to 10.812 Å (1.4%), while $a$ decreases from 9.611 Å to 9.546 Å (0.68%).
anisotropic lattice change by the Y doping may result from correlations of the relative strength of inter-chain and intra-chain coupling, as was suggested by Rayaprol et al. [17].

In the Sr$_3$Co$_2$O$_6$ structure, the parallel Co1-O-Co2 chains are separated by Sr$^{2+}$ ions and the chains are ordered in a triangular lattice in the $ab$ plane. The structure change by the Y doping thus indicates that the relative distance between the inter-chains is reduced and the intra-chain neighbor Co ions are slightly more separated along the $c$-axis. In turn, the intra-chain FM coupling is likely enhanced, and the inter-chain AFM coupling is somewhat weakened. Note that when $x$ goes to 0.4, the XRD peak looks remarkably broader, suggesting multiple peak splitting, determining that the solubility limit of Y is $x$ of 0.3 or slightly below at the synthesis condition.

### Table 1. The lattice and magnetic parameters for Sr$_{3-x}$Y$_x$Co$_2$O$_6$ ($x = 0, 0.1, 0.2, 0.3$).

| $x$  | a(Å)  | c(Å)  | c/a  | $T_{c1}$, $T_{c2}$(K) | $\Theta_c$(K) | $\mu_{eff}$($\mu_B$/F.u.) |
|------|-------|-------|------|-----------------------|----------------|----------------------------|
| 0    | 9.611 | 10.701| 1.113| 22, 9                  | 85             | 6.14                       |
| 0.1  | 9.602 | 10.753| 1.119| 16, 7                  | 62             | 5.79                       |
| 0.2  | 9.588 | 10.795| 1.126| 11, 4                  | 34             | 5.61                       |
| 0.3  | 9.546 | 10.812| 1.133| 4, 3                   | 9              | 5.52                       |

Figure 2 shows the $\chi(T)$ between 2 K and 50 K measured in a field of 5 kOe. The host Sr$_3$Co$_2$O$_6$ shows anomalies at 22 K ($T_1$) and 9 K ($T_2$) as reported recently by us [9]. The analogous compound Ca$_3$Co$_2$O$_6$ also shows a similar magnetic feature at $T_1$, to which a combined effect of the intra-chain FM ordering and the inter-chain AFM ordering was ascribed [18, 19]. The second peak ($T_2$) of Ca$_3$Co$_2$O$_6$ is indicative of a magnetic transition to the ferrimagnetic state [20]. The studies suggest that the host Sr$_3$Co$_2$O$_6$ and the analogous Ca$_3$Co$_2$O$_6$ share the almost common magnetic nature.

With alloying Y with Sr$_3$Co$_2$O$_6$, $T_1$ shifts to lower temperatures and disappear (>2 K) at $x$ of 0.3. $T_2$ is suppressed as well with the alloying; however $T_2$ is still visible at $x = 0.3$. The values of $T_1$ and $T_2$ are summarized in Table 1. The observations indicate that the Y doping has large influences on the magnetic behaviors of Sr$_3$Co$_2$O$_6$. In order to quantitatively analyze the effect, we applied the Curie-Weiss law to the paramagnetic regime of $\chi^{-1}(T)$, which is plotted in Figure 3. The analytical
The formula was \( \chi(T) = N_A \mu_{\text{eff}}^2 / 3\pi(T - \Theta_W) \), where \( N_A \) is the Avogadro constant, \( \Theta_W \) is the Weiss temperature, and \( \mu_{\text{eff}}^2 \) is the effective Bohr magneton. The parameters estimated by a least-squares fitting are summarized in Table 1.

The host \( \text{Sr}_3\text{Co}_2\text{O}_6 \) has \( \mu_{\text{eff}} \) of 6.14 \( \mu_B \) and \( \Theta_W \) of +85 K, implying that the intra-chain FM interaction is dominant in the magnetic ground state [9]. The \( \mu_{\text{eff}} \) is comparable with that of \( \text{Ca}_3\text{Co}_2\text{O}_6 \) (6.08 \( \mu_B \)) [21], indicating a large Landé factor \( g \) of 2.5 for \( \text{Sr}_3\text{Co}_2\text{O}_6 \) if \( d \) spins are the only magnetic source. As argued for \( \text{Ca}_3\text{Co}_2\text{O}_6 \) [22], the large Landé factor is a possible source of the Ising-like anisotropy of the Co spins. Here we found that \( \mu_{\text{eff}} \) goes to smaller by the Y doping in \( \text{Sr}_3\text{Co}_2\text{O}_6 \) from 6.14 \( \mu_B \) (\( x = 0 \)) to 5.52 \( \mu_B \) (0.3), and \( \Theta_W \) from 85 K (\( x = 0 \)) to 9 K (0.3). The results directly reflect the doping effect on the magnetic properties. Surprisingly, qualitatively comparable effect was observed by the Y doping to \( \text{Ca}_3\text{Co}_2\text{O}_6 \), implying indeed a common physics between the two compounds despite there being a large gap between the unit cell sizes. However, the changes occur much quickly with increasing the Y content in \( \text{Sr}_3\text{Co}_2\text{O}_6 \) than in \( \text{Ca}_3\text{Co}_2\text{O}_6 \) [13-15].

For \( \text{Sr}_3\text{Co}_2\text{O}_6 \), the 1/3 magnetization plateaus in \( M \) vs. \( H \) curve is perhaps the most distinguishable...
feature [9]. To shed more light on the magnetization nature, the Y doped Sr$_3$Co$_2$O$_6$ are studied as well at 5 K (Figure 4). With increasing the Y content, the plateau is gradually smeared out and almost disappears at $x = 0.3$. The suppression is clearly coupled with the decreasing of the saturated magnetic moment ($M_s$); the $M_s$ at $x = 0.3$ is 1.8 $\mu_B$/f.u, which is approximately half of the $M_s$ at $x = 0$.

The magnetization plateaus of Ca$_3$Co$_2$O$_6$ was interpreted in a framework either of a quantum tunneling of the magnetization [21,23] or a field-driven transition between the spin-up and spin-down chains [24]. Vidya et al. proposed that additional electrons caused by the Y doping occupy the interstitial sites or are uniformly distributed to all constituents, suggesting a possible new electronic state consists of the low spin Co$^{4+}$ and the high-spin Co$^{2+}$ [12]. Besides, Sekimoto et al. and Kim et al. suggested that the Y-doping may result in a spin configuration of $S = 0$ (Co$^{3+}$) and $S = 3/2$ (Co$^{2+}$) [13,14].

For the results for the Y doped Sr$_3$Co$_2$O$_6$, two interpretations may be possible at this moment. The first one is that the doped Y gives rise to the spin configuration of $S = 0$ for Co1 (Co$^{3+}$) and $S = 3/2$ for Co2 (Co$^{2+}$) as just mentioned in Ref. 13 and 14. The substantial change in the magnetization supports the scenario. The other one is that the Ising-type magnetic anisotropy of Co2 of the host Sr$_3$Co$_2$O$_6$ is in fact very weak, and the Y-doping strengthens the magnetic anisotropy, accounting for the gradual decrease of $M_s$. A conclusive judge will be given in future study.

In summary, we studied the Y-doping effect on Sr$_3$Co$_2$O$_6$ by measurements of magnetic susceptibility and magnetization, followed by comparison with the Y-doping effect on the analogous oxide Ca$_3$Co$_2$O$_6$. The magnetically ordered structure was altered in a similar way for the Ca compound; however the changes occur much quickly with increasing the Y content. The observation may reflect deference of degree of the magnetic anisotropy of the Co spins among the Ca and Sr oxides; further theoretical studies may help to reveal the origin of the possible deference of the magnetic anisotropy.

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