The Effect of Element Substitution on Thermoelectric Properties of the One-dimensional Homologous Series $A_{n+2}Co_{n+1}O_{3n+3}$

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We studied the effect of Zn and La doping on the thermoelectric properties of polycrystalline samples of the $n=2$ and 3 members of the homologous series $A_{n+2}Co_{n+1}O_{3n+3}$, where A represents an alkaline-earth metal. The Seebeck coefficient of the $n=3$ samples decreased with increasing the Zn content, but otherwise was little affected with Zn and La doping. Resistivity decreased systematically with Zn and La doping except for $Sr_4Co_{3-y}Zn_yO_9$ ($n=2$). Among all studied samples, $Sr_{3.2}La_{0.8}Co_3O_9$ exhibited the largest power factor, which is 1.3 times larger than that of the non-doped $n=2$ sample, and 3.0 times larger than the non-doped $n=1$ sample.
Key words: thermoelectric properties, Co oxide, $A_{n+2}Co_{n+1}O_{3n+3}$ homologous series

1. INTRODUCTION

In 1997, it was reported that $NaCo_2O_4$ possesses a large thermopower and low resistivity at the same time, which makes this material an attractive candidate for thermoelectric applications [1]. The excellent thermoelectric performance of this material was further confirmed by measuring the dimensionless figure of merit ZT defined as $ZT=S^2T/\rho\kappa$, where S is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity, and T temperature [2,3]. This finding stimulated an extensive investigation of thermoelectric properties of other cobalt oxides, and it was found that $Ca_3Co_4O_9$ [4-6] and $Bi_2Sr_2Co_2O_9$ [7] also show good thermoelectric performance. These cobalt oxides share a common structural unit, the CdI_2-type CoO_2 plane, which consists of edge-sharing CoO_6 octahedra forming a triangular lattice of Co. It was pointed out that $(La,Sr)CoO_3$ may also be a good thermoelectric material at around room temperature [8,9], the structure of which consists of corner-sharing CoO_6 octahedra forming a three-dimensional network. However, all these materials cannot be used at high temperature because the layered cobalt oxides decompose at around 1100 K and the Seebeck coefficient of $(La,Sr)CoO_3$ decreases rapidly above about 500 K due to a spin state transition.

Recently, Mikami *et al.* claimed that $Ca_3Co_2O_6$, which is chemically stable up to at least 1300 K [10], has a significant potential as a thermoelectric material at high temperature [11]. They reported that ZT of a single crystal reached 0.15 at 1073 K, and estimated the ZT value at 1300 K to be 0.44 by extrapolating their data. $Ca_3Co_2O_6$ has been already known for decades [10,12], and attracted considerable attention especially on its peculiar magnetic properties [13,14]. It is the first member ($n=1$) of a homologous series that is expressed as $A_{n+2}Co_{n+1}O_{3n+3}$ (A=Ca, Sr, Ba), and more generally $A_{n+2}B'B_nO_{3n+3}$ (B'=Co, Ni, Cu,

Zn, ...; B=Co, Ir, Pt, ...) with B' and B=Co [15]. The unit cell of $A_{n+2}Co_{n+1}O_{3n+3}$ contains one CoO_6 trigonal prism and n CoO_6 octahedra. Unlike the Co oxides mentioned above, the CoO_6 units are sharing the face and are connected one-dimensionally. The chains are separated by an alkaline-earth metal and each chain is surrounded by six equally spaced chains forming a triangular lattice in the ab plane.

Although the thermoelectric performance reported for $Ca_3Co_2O_6$ by Mikami *et al.* is already considerably large, it still fails to meet the criterion for practical use as a thermoelectric material, $ZT>1$. In previous studies, we measured systematically the thermoelectric and magnetic properties of polycrystalline samples that correspond to $n=1-5$ [16,17]. We observed that the $n=2$ compound, $Sr_4Co_3O_9$, exhibited the lowest resistivity among all studied samples above 300 K. Moreover, the $n=2$ sample exhibited the largest power factor, S^2/ρ, which is 2.3 times larger than that of the $n=1$ sample. In a more recent work, we studied the effect of partially substituting Zn for Co of $Ca_3Co_2O_6$, and observed an increase in S^2/ρ by a factor of 1.7 when 5% of the Co ions are replaced by Zn [18]. Furthermore, the comparison with other reports led us to conclude that the CoO_6 octahedron is an important structural unit for the good thermoelectric properties at high temperatures of this compound.

In the present work, we extend our study to the effect of Zn doping to the $n=2$ and 3 members of the homologous series, because the non-doped $n=2$ compound exhibited a larger power factor than $n=1$. We also studied the effect of replacing the alkaline-earth metal by La, which is another way to modify the compound without altering the CoO_6 octahedron.

2. EXPERIMENTAL

We used polycrystalline samples in this study,

which were prepared similarly to the method used in our previous studies [16,18]. X-ray diffraction measurements were carried out with a Rigaku diffractometer using Cu Kα radiation to confirm the phase purity. Resistivity was measured with a four-probe method. The Seebeck coefficient was measured using the Seebeck effect measurement system of MMR Technologies Inc. between 90 and 400 K, and using ZEM2-M10NI of ULVAC between 300 and 1073 K.

3. RESULTS AND DISCUSSION

Zn-doped single-phased samples were obtained in the range of $y \leq 0.3$ and $y \leq 0.15$ for $Sr_4Co_{3-y}Zn_yO_9$ ($n=2$) and $Sr_5Co_{4-y}Zn_yO_{12}$ ($n=3$), respectively, as was confirmed using x-ray diffraction. The lattice parameters a and c both increased with the Zn content, indicating that the Co sites are indeed substituted by Zn which has a larger ionic radius. On the other hand, doping La to the $n=2$ compound was very difficult. We prepared samples of $Sr_{4-x}La_xCo_3O_9$ with $x=0.03$, 0.05, 0.1, and 0.8, and varied the sintering condition for a wide range. However, the synthesis of a single-phased sample was successful only for $x=0.8$, i.e., only when 20% of Sr were replaced by La. It is interesting here to mention that a study on La doping to the $n=\infty$ member of the present homologous series reports that only $Ba_{0.8}La_{0.2}CoO_3$ could be successfully prepared, and doping a smaller amount of La resulted in multi-phased samples [19]. In contrast to $n=2$, doping a small amount of La to the $n=3$ compound was more successful. Figure 1 shows the XRD patterns of the La doped $n=3$ samples, $Sr_{5-x}La_xCo_4O_{12}$ ($x=0$, 0.03, 0.1, 0.2, and 0.3). All peaks of the $x=0$ sample can be indexed by a hexagonal unit cell consistent with the literature [15] and no impurity phase was detected for samples with $x \leq 0.2$. However, a small impurity peak was observed for the $x=0.3$ sample, which is marked with an arrowhead ($\blacktriangledown$). We attempted also the preparation of a $n=3$ sample by replacing 20% of Sr by La, the "magic number" of the $n=2$ and ∞ compounds, but failed to obtain a single-phased sample. The lattice parameters determined from the data of Fig. 1 decreased with the La content up to $x=0.2$. This indicates that Sr ions are indeed substituted by La which has a smaller ionic radius.

Figure 2(a) shows the temperature dependence of Seebeck coefficient of the Zn doped $n=2$ samples, $Sr_4Co_{3-y}Zn_yO_9$. The Seebeck coefficient of all samples was positive in sign for the whole temperature range, and increased with temperature. The Seebeck coefficient was almost unaffected by Zn doping and was similar to the non-doped sample in a wide range of temperature. In our previous study on the $n=1$ compound, we concluded that replacing Co of the CoO_6 octahedron with a foreign element results in a large decrease of the Seebeck coefficient while substituting for Co of the CoO_6 trigonal prism is less harmful by comparing our results of Zn doping
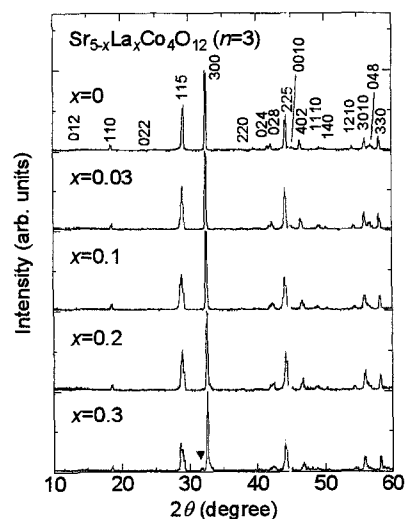

Fig. 1. Powder x-ray diffraction patterns of $Sr_{5-x}La_xCo_4O_{12}$ ($0 \leq x \leq 0.3$).

and the data of other element substitution reported in the literature [18]. For the $n=1$ compound, Zn is claimed to substitute for Co in the prism site [20]. Probably, the Zn ions doped into the $n=2$ compound similarly substitute only for the prism site, and we think that this is the reason why the Seebeck coefficient was almost unaffected by Zn doping.

On the other hand, the Seebeck coefficient decreased with doping Zn to the $n=3$ compound, as shown in Fig. 2(b). A possible explanation of this result is that some Zn ions substituted the octahedron site in the $n=3$ compound. As mentioned above, only the number of CoO_6 octahedron increases with increasing n, and we think that some of the Zn ions may start to substitute for the
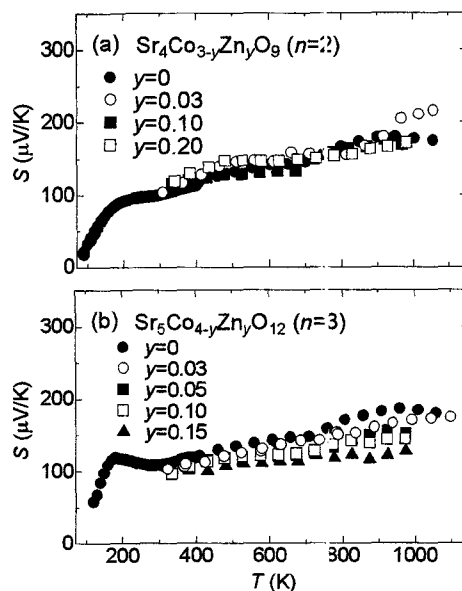

Fig. 2. Seebeck coefficient of (a) $Sr_4Co_{3-y}Zn_yO_9$ ($n=2$) and (b) $Sr_5Co_{4-y}Zn_yO_{12}$ ($n=3$) plotted as a function of temperature.
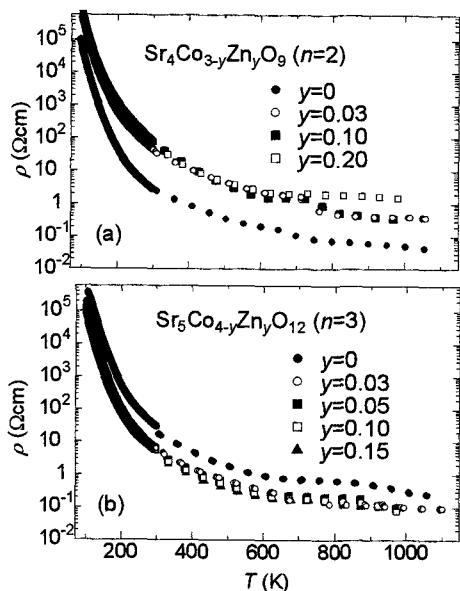
Fig. 3. Temperature dependence of the electrical resistivity of (a) $Sr_4Co_{3-y}Zn_yO_9$ (n=2) and (b) $Sr_5Co_{4-y}Zn_yO_{12}$ (n=3).

Fig. 4. Seebeck coefficient of (a) $Sr_{4-x}La_xCo_3O_9$ (n=2) and (b) $Sr_{5-x}La_xCo_4O_{12}$ (n=3) plotted as a function of temperature.

octahedron site when the number of CoO_6 octahedron is large. Moreover, it is interesting to note that unlike the n=1 and 2 compounds, the unit cell of the n=3 compound includes a CoO_6 octahedron that is not adjoining a CoO_6 trigonal prism. Because of this structural difference, the substitution of Zn for Co of the octahedron site might be easier. A detailed structural analysis is necessary to confirm this scenario.

Figures 3(a) and (b) show the temperature dependence of resistivity of the Zn doped n=2 and 3 samples, respectively. The two systems showed an opposite behavior with Zn doping, i.e., ρ of the n=2 compound increased with Zn doping while that of n=3 decreased. Because ρ of the n=1 compound decreased with Zn doping [18], only the n=2 system behaves differently, the reason of which is unclear at present.

Figure 4(a) shows the temperature dependence of Seebeck coefficient of the $Sr_{4-x}La_xCo_3O_9$ samples (n=2). The Seebeck coefficient of the x=0.8 sample was almost the same as that of the non-doped one except for temperatures higher than 873 K. Similarly, the Seebeck coefficient of the n=3 compound did not change much with La doping, as is displayed in Fig. 4(b). This behavior can be well understood by the same assumption that the Seebeck coefficient is less affected if the CoO_6 octahedra are not modified.

Figures 5(a) and (b) show the temperature dependence of resistivity of the La doped samples. For both n=2 and 3, ρ decreased with increasing the La content. In particular, $Sr_{3.2}La_{0.8}Co_3O_9$ showed the lowest ρ among all samples studied in this work. On the other hand, it was reported that substitution of La for Ca of $Ca_3Co_2O_6$ (n=1) resulted in a change to the opposite direction, i.e., the resistivity increased [21]. This may be related

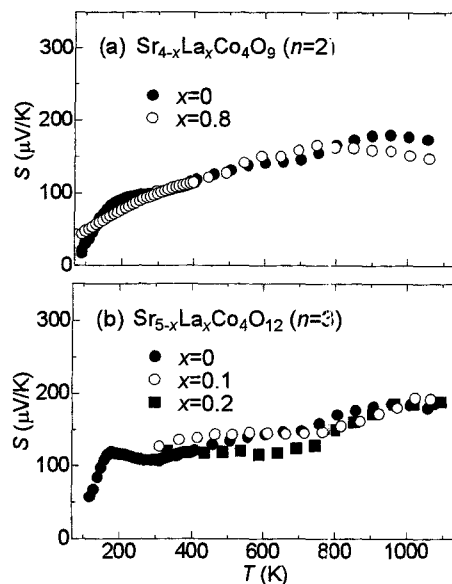to the change of the c axis length with La doping. For our n=2 and 3 samples, the lattice constant c decreased with increasing the La content. On the other hand, it was reported that the c axis length of the n=1 compound increased with La doping [21]. Note here that the A site element of the n=1 compound is Ca, while it was necessary to change it to Sr to obtain single phased n=2 and 3 samples [16]. The change in the c axis length with La doping can be hence easily understood, because the ionic radius of Sr^{2+}, La^{3+}, and Ca^{2+} decreases in this order. Due to the large anisotropy of resistivity [11], the resistivity along the chain direction has the dominant contribution to the observed resistance. When the c axis length decreases, the Co $3d$ and O $2p$ orbitals would have a larger overlap, and the resistivity is expected to decrease. Hence, the observed change in resistivity with La doping is consistent with the change of c axis length.

Figure 6 shows the temperature dependence of the power factor of all samples studied in this work. The power factors of all samples were small at room temperature, but increased with temperature. $Sr_{3.2}La_{0.8}Co_3O_9$ exhibited the largest power factor among all samples, which was 1.3 times larger than that of the non-doped n=2 sample. Moreover, it is 3.0 times larger than that of $Ca_3Co_2O_6$. The power factor of the n=2 sample decreased with Zn doping due to the increase of ρ (Fig. 3(a)). On the other hand, for n=3, La and Zn doping both increased the power factor, because S was almost unaffected while ρ decreased.

4. CONCLUSION

We prepared polycrystalline samples of $(Sr_{4-x}La_x)(Co_{3-y}Zn_y)O_9$ (n=2) and $(Sr_{5-x}La_x)(Co_{4-y}Zn_y)O_{12}$ (n=3), and studied the
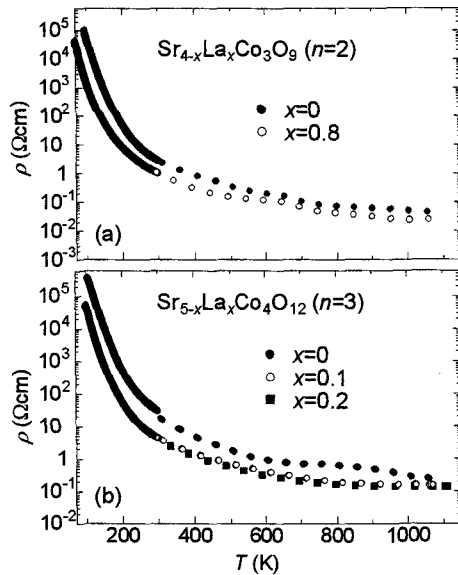
Fig. 5. Temperature dependence of the electrical resistivity of (a) $Sr_{4-x}La_xCo_3O_9$ ($n=2$) and (b) $Sr_{5-x}La_xCo_4O_{12}$ ($n=3$).
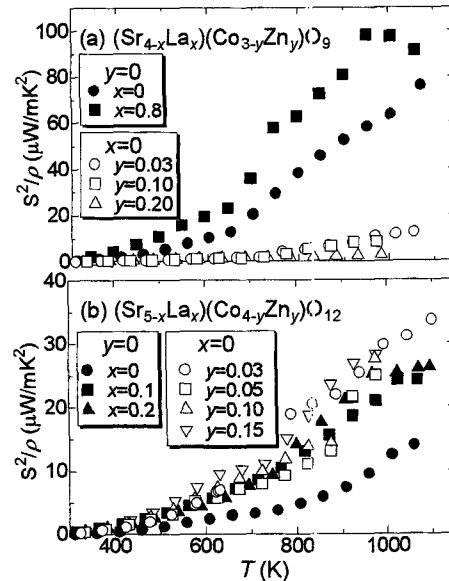

Fig. 6. Temperature dependence of the power factor of (a) $(Sr_{4-x}La_x)(Co_{3-y}Zn_y)O_9$ ($n=2$) and (b) $(Sr_{5-x}La_x)(Co_{4-y}Zn_y)O_{12}$ ($n=3$).

electrical resistivity and the Seebeck coefficient. Resistivity decreased with the element substitution, except for the case of doping Zn to the $n=2$ compound ($Sr_4Co_{3-y}Zn_yO_9$). On the other hand, the Seebeck coefficient was almost unaffected by both Zn and La doping within the studied range of composition, except for doping Zn to the $n=3$ compound ($Sr_5Co_{4-y}Zn_yO_{12}$). The La doped $n=2$ sample, $Sr_{3.2}La_{0.8}Co_3O_9$, exhibited the largest power factor among all samples of this work, and was 1.3 times larger than that of the non-doped $n=2$ sample, and 3.0 times larger than the non-doped $n=1$ sample.

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