Crystalline Phases and Thermoelectric Properties of Ca₂Co₂O₅-Based Solid Solutions

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As an attempt to obtain a clue to design perovskite-related oxide thermoelectrics, a part of Co^{3+} ions in $Ca_2Co_2O_5$ was substituted with Ni^{2+}, Al^{3+}, Fe^{3+}, and Sn^{4+}. The structure of $Ca_2Co_2O_5$, an oxygen-deficient perovskite structure, was maintained upon introducing Al^{3+}, while it transformed to brownmillerite structure by incorporating Fe^{3+} or Sn^{4+} and to $Ca_3Co_2O_6$ structure by Ni^{2+}. The phase transformation behavior was qualitatively explained based on the consideration of the ionic radii and charges of the substituting ions. The thermoelectric performance of the $Ca_2Co_2O_5$-structured samples and brownmillerite-structured samples did not show very large difference regardless of the nature of the substituting ions. On the other hand, the $Ca_3Co_2O_6$-structured sample exhibited a marked decrease in the electrical conductivity, causing a deteriorating effect on the power factor. Brownmillerite structure seemed to be superior to $Ca_2Co_2O_5$-structure as the host structure for the material design of perovskite-related oxide thermoelectrics because of its structural stability.

Key words: $Ca_2Co_2O_5$, perovskite, brownmillerite, thermoelectric, phase transformation

1. INTRODUCTION

Since the discovery of $NaCo_2O_4$[1] and $Ca_3Co_4O_9$[2], cobalt-containing oxides and solid solutions have attracted much attention as potential candidates of high-performance thermoelectrics. $Ca_2Co_2O_5$, which will be referred to as "225" in this paper, is one of such compounds, and has a oxygen-deficient perovskite structure in which all the Co^{3+} ions are located in the basal plane of a 5-fold coordinated pyramid[3]. The linkage of the pyramids is schematically shown in Fig. 1 together with the arrangement found in regular perovskites.
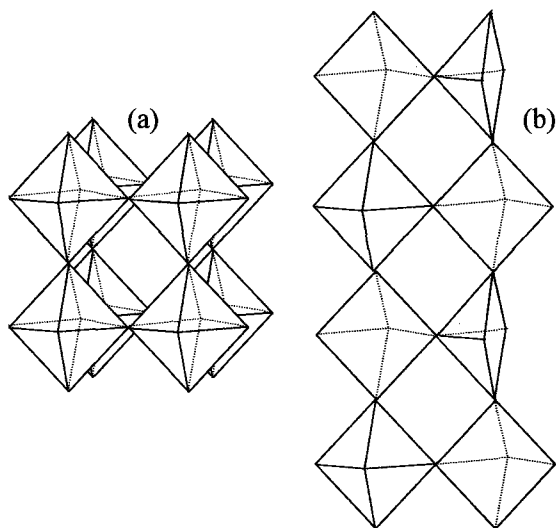
Reports on the thermoelectric properties of the 225-related compounds, however, are quite limited. Li et al.[4] reported that the substitution of a part of Ca^{2+} in the 225-compound with Bi^{3+} produced a mixture of 225-phase and $Bi_2Ca_2Co_2O_x$, and the Seebeck coefficient and the electrical conductivity increased while the thermal conductivity decreased, resulting in an increase in the figure of merit. Kobayashi et al.[5] reported that $Ca_2(Co, Al)_2O_5$ solid solutions had brownmillerite structure and the substitution of Ca^{2+} with La^{3+} converted the sign of the Seebeck coefficient from positive to negative. Brownmillerite structure is also an oxygen-deficient perovskite structure in which half the B ions occupy 4-fold coordination sites and the rest 6-fold sites, as schematically shown in Fig. 2.
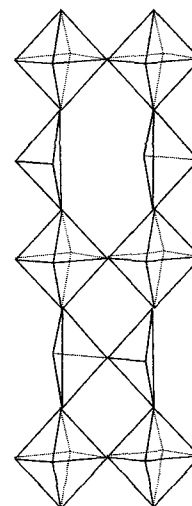

Fig. 2 Schematic representation of the linkage of the coordination polyhedra around "B ions" in brownmillerite.

Fig.1 Schematic representation of the linkage of the coordination polyhedra around "B-ions" in (a) perovskite and in (b) 225-structures.

These findings imply that a partial substitution of the ions in the 225-compound may affect both crystal structure and the thermoelectric properties.   In the present work, for the purpose of obtaining some clues to design high-performance thermoelectrics from perovskite-related compounds, the effects of a partial substitution of the Co^{3+} ion on the crystalline phase and the thermoelectric properties were investigated.

2. EXPERIMENTAL

2.1 Sample preparation

The chemical formulae investigated in this work are expressed as $Ca_2Co_{1.8}M_{0.2}O_{5\pm\delta}$, where M = Ni^{2+}, Al^{3+}, Fe^{3+}, and Sn^{4+}.   Mixtures of pertinent amounts of $CaCO_3$, $CoCO_3$, NiO, Al_2O_3, Fe_2O_3 and SnO_2 of analytical grade purities were calcined at 1173K for 3 hours in a stagnant oxygen atmosphere in an electric furnace (Marusho-Denki, SPM 65-16V).   The calcined powders were pressed into pellets of 20mm in diameter and were sintered at 1273, 1353, and 1423K for 6 to 12 hours in a stagnant oxygen atmosphere.

2.2 Characterization

The calcined and sintered specimens were subjected to an X-ray diffraction analysis using $CuK\alpha$ radiation to identify crystalline phases.   The Seebeck coefficient and the electrical conductivity were measured in a temperature range from room temperature to 1000K in a flow of oxygen to suppress self reduction of metal ions during the measurements.

3. RESULTS AND DISCUSSION

3.1 Crystal structures

Table I summarizes the effects of the heat-treatment temperature and the kind of the dopant on the crystalline phase.   The 225-structure is stable up to 1353K for non-doped and Al-doped samples, and it starts to transform to $Ca_3Co_2O_6$ (326)-structure at 1423K.   Ni-doped sample readily transforms to 326-structure and Fe- and Sn-doped samples transform to brownmillerite structure.   In the 326-structure, Ca^{2+} ions occupy the 8-fold coordination sites and all the Co^{3+} ions are located in the 6-fold coordination sites[6].

Table I   Effects of the heat-treatment temperature and the kind of dopant on crystalline phase.

Dopant	Temperature, K			
	1173	1273	1353	1423
non-doped	225	225	225	225+326
Al^{3+}	225	225	225+U	225+326
Ni^{2+}	225	326	326	326
Fe^{3+}	225	BM	BM	BM
Sn^{4+}	225	225+BM	BM+U	BM

225: $Ca_2Co_2O_5$, 326: $Ca_3Co_2O_6$
BM: brownmillerite, U: unidentified

The structural transformation from 225- to 326-structure for non-doped sample may be explained in terms of the self reduction of Co^{3+} to Co^{2+} at high temperatures. Co^{2+} ions statistically occupy the 8-fold coordination site with Ca^{2+} ions, forming $(Ca^{2+}{}_2Co^{2+}{}_{0.4})Co^{3+}{}_{1.6}O_{4.8}$.   For Ni-doped sample, because of the 2+ valence and its larger ionic radius (83pm) compared with that of Co^{3+} (75pm), Ni^{2+} might occupy the 8-fold site in the 326-structure.

The transformation to brownmillerite structure in the Sn-doped sample may be accounted for the larger ionic radius of Sn^{4+} (83pm) and higher valence. Sn^{4+} ions might prefer the 6-fold coordination site to the 5-fold site, destabilizing 225-structure against the brownmillerite structure.

In the present work, the Al-doping does not affect the stability of the 225-structure very much, in spite of the report of Kobayashi et al.[5] claiming $Ca_2(Co, Al)_2O_5$ crystallizes into the brownmillerite.   That is probably because the amount of Al^{3+} ion is smaller in this work.   It may be the case that smaller ion than Co^{3+}, such as Al^{3+} (68pm), does not disturb much the stability of 225-structure while larger ion such as Fe^{3+} (79pm) is favored by the brownmillerite structure.

Fig. 3 shows the examples of the X-ray diffraction patterns of 225-, 326-, and the brownmillerite-structured samples.
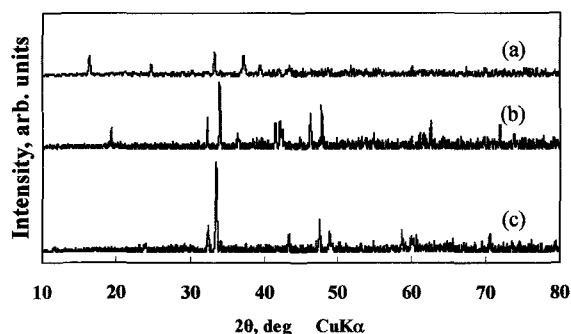

Fig. 3 X-ray diffraction patterns of (a) non-doped sample sintered at 1273K, (b) Ni-doped / 1273K, and (c) Fe-doped / 1353K, showing 225-, 326-, and brownmillerite structures, respectively.

3.2 Thermoelectric properties

Fig. 4 shows the temperature dependence of the electrical conductivities of the present samples.   In the figure, the data of non-doped 225 compound in Li and coworkers' paper[4] are plotted for comparison.   Ni-doped sample shows significantly low conductivities.   Other samples show almost comparable conductivities regardless of the structure.   The low electrical conductivity of Ni-doped sample may be coming from its 326-structure[6] in which the conduction path is one-dimensional.

Li and coworkers' non-doped sample showed higher conductivity than our sample, probably due to higher packing density.
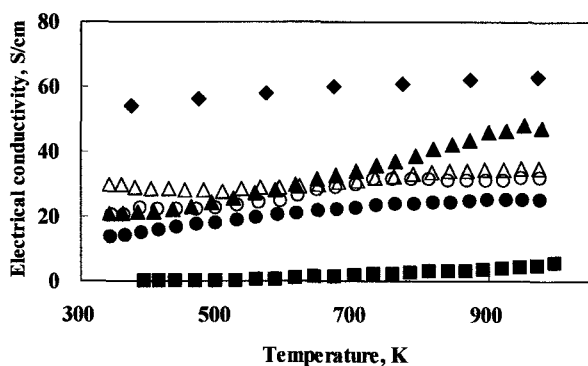
Fig.4 Temperature dependence of the electrical conductivity; $\bigcirc$: non-doped, $\bullet$: Al-, $\triangle$: Sn-, $\blacktriangle$: Fe-, $\blacksquare$; Ni-doped samples and $\blacklozenge$ are the data from Li et al[4].

Fig.5 shows the temperature dependence of the Seebeck coefficients.   All the samples exhibit positive Seebeck coefficients.   Here again, Ni-doped sample shows markedly high Seebeck coefficient, which may be characteristic to the 326-structure[6].   The thermopowers of other samples fall in a similar range to each other.
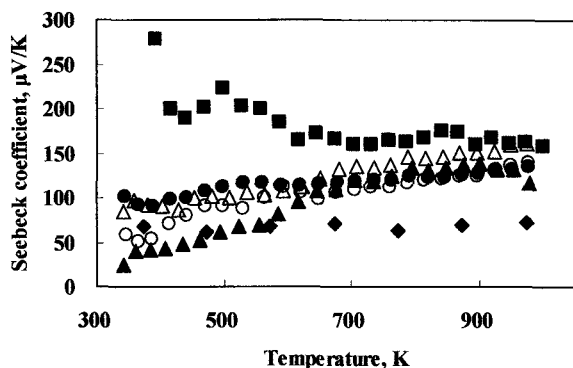

Fig. 5 Temperature dependence of the Seebeck coefficient.   Keys are the same as those in Fig. 4.

Fig. 6 shows the temperature dependence of the power factors.   Fe- and Sn-doped samples show higher values than the non-doped sample.   However, this does not immediately mean that the brownmillerite structure is thermoelectrically better than the 225-structure because not only the crystal structure but also the dopant ions might affect the thermoelectric properties.   At least, however, it has been shown in this work that the brownmillerite structure is more stable than the 225-structure against doping and may be the more suitable host to explore perovskite-related oxide thermoelectrics from.
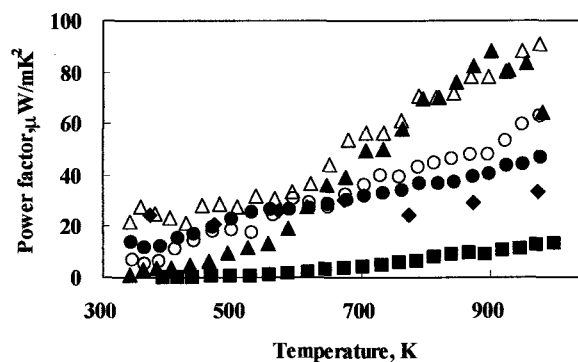

Fig. 6 Temperature dependence of the power factor.   The keys are the same as those in Figs. 4 and 5.

4. SUMMARY

Substitution effects of Co^{3+} with Al^{3+}, Ni^{2+}, Fe^{3+}, and Sn^{4+} in $Ca_2Co_2O_5$ on the crystalline phase and thermoelectric properties have been elucidated. Ni^{2+} substitution promoted the phase transformation to $Ca_3Co_2O_6$-structure, and Sn^{4+} substitution promoted the phase transformation to brownmillerite structure.   These changes were interpreted from the valence and ionic radius of the substituting ion. Fe^{3+} promoted the transformation to brownmillerite, while Al^{3+} maintained the stability of $Ca_2Co_2O_5$ structure.

The thermoelectric performance of Ni-doped sample showed low electrical conductivity and high Seebeck coefficient.   Fe- and Sn-doped samples showed roughly similar performance to the non-doped one.   Brownmillerite-structured compounds seem to be preferable than the $Ca_2Co_2O_5$-structured compounds for the material design of perovskite-related thermoelectrics because of its structural stability against phase transformation upon doping.

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