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Thermoelectric performances of perovskite transition-metal oxides at high temperature

Delphine Flahaut*[1,2], Christophe Goupil[1], Sylvie Hébert[1], Sébastien Lemonnier[1], Jacques Noudem[1], Antoine Maignan[1], and Ryoji Funahashi[2]
Laboratoire CRISMAT, UMR 6508, CNRS/ENSICAEN, 6, boulevard Maréchal Juin, 14050 Caen cedex-France
National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
*Fax: +81-72-751-9622, e-mail: delphine.flahaut@aist.go.jp

Abstract

A sign change of the thermoelectric power (TEP) revealed by Seebeck (S) measurements was induced by tetravalent substitutions at the A- or B-site in the $LaCoO_3$ and $PrCoO_3$ perovskite-type oxides. This opened a new route to generate n-type and p-type legs for thermoelectric devices.

In the present paper, we report on the S sign change induces by chemical substitution. The creation of Co^{2+} or Co^{4+} in the Co^{3+} matrix involves an $S < 0$ or $S > 0$, respectively. On the other hand, a more complicated behavior is induced for the $LaCo_{0.99}Ir_{0.01}O_3$ compound, which exhibits a negative and small value. Moreover, the $PrNi_{0.1}Co_{0.9}O_3$ compound exhibits a ZT value of 0.016 300K being close to the value reported by Migiakis et al. for $LaNi_{1-x}Co_xO_3$ (x=0.2).

We have also focused our study on the high temperature dependence of the Seebeck coefficient. In this temperature range, the $LaCoO_3$ perovskite substituted derivatives exhibit a constant S value of ~20-30 μV.K^{-1} for all compounds. This unique value is obtained independently of the nature of charge carrier. This can be explained by the Co^{3+} spin state transition towards HS which is completed at 500K and leads to a more conducting behavior; a similar result is also observed in the $PrCo_{1-x}Ni_xO_3$ series.

Keyword: thermoelectric power, cobalt oxide, cationic substitution, perovskite

Introduction

Potential thermoelectric materials have been found among transition-metal oxides, especially in layered cobaltites, which are strongly correlated electron systems and develop peculiar physical properties [1-2]. Moreover, these materials are made of non-toxic and abundantly available elements, which are stable up to 1000K. In cobaltites, the cobalt cation is being able to adopt several oxidation (for instance Co^{3+}/Co^{4+}) and spin states (LS: $t_{2g}^6e_g^0/t_{2g}^5e_g^0$; IS: $t_{2g}^5e_g^1/t_{2g}^4e_g^1$; HS: $t_{2g}^4e_g^2/t_{2g}^3e_g^2$). On the one hand, the valency of the cobalt (v~+3.5) is playing an important role in the room temperature TEP [3] and more precisely the presence in the matrix of LS Co^{3+}/Co^{4+}. On the other hand, the spin degeneracy and the ration of Co^{3+} and Co^{4+} affect S [3].

Therefore, a ZT value >>1 must be reached for application (Z the figure of merit $Z = \frac{S^2\sigma}{\kappa}$, S: Seebeck coefficient, κ: thermal conductivity, σ: electrical conductivity). For instance, the layered $Ca_3Co_4O_9$ compound shows a large and promising figure of merit such as ZT=0.87 at 973K [4].

In the three-dimensional (3D) perovskite, the thermoelectric properties are also interesting. $LaCoO_3$ is still studied for its two thermally assisted transitions for the Co^{III} [5-7] species. Its ground state is a non-magnetic insulator where the cobalt is trivalent LS. Around 100K, a transition from LS to IS Co^{III} is observed, and for T>500K all the IS species are converted to HS. It must be also mentioned that $LaCoO_3$ exhibits S(300K)~600μVK^{-1}. This family can generate p- and n-type thermomaterials by using cationic substitution [8,9]. The $PrCo_{1-x}Ni_xO_3$ series has also been studied in this paper for x≤0.3. Actually, Migiakis et al. [10] have reported a ZT~0.02 value at 300K in $LaCo_{0.8}Ni_{0.2}O_3$, being much larger than that of $LaCoO_3$ ZT=1.5*10^{-4}. This ZT value approaches the value obtained for Na_xCoO_2 [2] compound. So mixing an insulator-like compound with a large S (like $LaCoO_3$) and a metallic compound of small S (as $LaNiO_3$) could be a new route to obtain TE materials.

In the present paper, we report on the properties of different 3D cobaltites to study their potentiality as p- and n-type TE materials. Seebeck coefficient measurements have been performed at high temperature on these compounds.

Experimental

Polycrystalline samples of $LaCoO_3$, $La_{0.99}A_{0.01}CoO_3$ (A=Ce, Ti), $LaCo_{0.99}Ir_{0.01}O_3$, $La_{0.98}Sr_{0.02}CoO_3$ and $LaCo_{0.995}Ga_{0.005}O_3$ were prepared via solid-state reaction in air. The powders were heated at 1000°C for 10 hrs and at 1150°C for 10h. After pressing, the bars were heated again at 1250°C for 20 hrs.

Ceramic samples of $PrCo_{1-x}Ni_xO_3$ (x=0.1; 0.2 and 0.3) have been synthesized by the same way.

The structures were characterized at room temperature (RT) by using a Philips X-ray diffractometer using CuKα. Electron diffraction (ED) and energy dispersive spectroscopy (EDS) investigation were carried out at RT with a JEOL 200 CX electron microscope equipped with a KEVEX analyser.

Resistivity data were collected with the four-probe technique. The Seebeck coefficient (S) was measured by using a steady-state method. Two apparatus were used depending on the temperature range ($T \leq 320K$, $T \geq 300K$). The thermoelectric power measurements are limited to a resistance of 10^5 Ohm.

Results

I Structural characterization

All the $La_{1-x}A_xCo_{1-x}B_xO_3$ compositions are single phase as determined by x-ray powder diffraction and transmission electron microscopy (diffraction) except for the compounds substituted by 1% of Ce which shows some CeO_2 traces. All these compounds crystallize in a slightly distorted perovskite which is indexed with the rhombohedral (R-3c) structure. For such small levels of substitutions, the cell parameters are almost unchanged. According to the very small content of dopant, the accurate cationic composition can not be determined. Nonetheless, we can check the cationic ratio La/Co~1.

The $PrCo_{1-x}Ni_xO_3$ series are also single phase and crystallize in an orthorhombic perovskite (Pnma).

II Thermoelectric properties at T<300K

$LaCoO_3$

At RT, the S value of $LaCoO_3$ is very large and positive $S=600\mu VK^{-1}$ [7], the transport is governed by holes in small concentration. A sign change of S can be obtained when tetravalent cations are substituted at the A-site (Ce^{4+}or Th^{4+}) or at the B-site (Sn^{4+} or Ti^{4+}) [8-9]. Accordingly, the nature of the charge carriers can be changed from "hole" for $LaCoO_3$ to "electron" in the substituted compounds.

This is illustrated by the S(T) curves in Figure 1. For all those compounds, the S(T) (Fig.1) curves are found to be nearly temperature independent in the T range of the measurements (up to 320K). The high value of S below 300 K for $LaCoO_3$ (640 μVK^{-1}) implies a near stoichiometric composition with a cobalt oxidation state of 3.0009. This value has been calculated from the Heikes formula. The S(T) curves (Fig.1) of the substituted compounds with tetravalent cations show that we are able to change the conduction mode by cationic substitutions. S reaches $-302\mu V.K^{-1}$ for $La_{0.99}Ce_{0.01}CoO_3$ and $-269\mu V.K^{-1}$ for $La_{0.995}Ti_{0.005}CoO_3$. The sign change suggests strongly that the nature of the charge carriers goes from hole-like to electron-like. On the other hand, an isoelectronic substitution, with non magnetic Ga^{3+} cation (d^0), does not create any charge carriers Co^{4+} or Co^{2+}. Nonetheless, it induces the partial destruction of cooperative orbital order of Co^{3+} IS e_g orbitals. This could explain the small decrease of S value, $S_{300K}=470$ $\mu V.K^{-1}$. Moreover, an aliovalent substitution with Sr^{2+} creates Co^{4+} in the Co^{3+}-O-Co^{3+} network. The increase in hole concentration induces, in that case, a large decrease of S value, $S_{300K}=332\mu VK^{-1}$. Actually, a Ga^{3+} or Sr^{2+} substitution do not induce change in the S sign. Nonetheless, the behavior of $LaCo_{0.99}Ir_{0.01}O_3$ is different from the others. First of all, the Ir cation can be tri- or tetravalent with the $5d^6$ or $5d^5$ electronic configuration, respectively. Maybe, we have to consider the fact that the d level is half-filled to explain the value of $S_{300K}=-53$ μVK^{-1}.

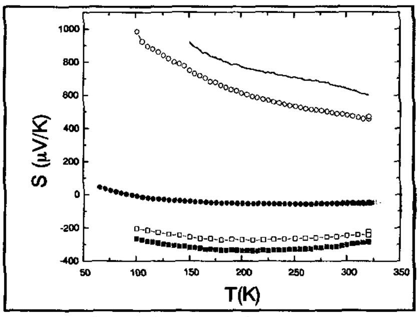

Figure 1: Seebeck coefficient versus temperature (100K<T<300K) curves for the $LaCoO_3$ (line), $LaCo_{0.995}Ga_{0.005}O_3$ (open circles), $LaCo_{0.99}Ir_{0.01}O_3$ (closed circles), $La_{0.99}Ti_{0.01}CoO_3$ (open squares) and $La_{0.99}Ce_{0.01}CoO_3$ (closed squares).

$PrCo_{1-x}Ni_xO_3$

This study was motivated by the fact that the transition temperature of the thermally assisted spin state transition in $LnCoO_3$ is increased when the lanthanide size is decreased [11] which is the case as one goes from La^{3+} to Pr^{3+}. Moreover, Migiakis et al. [10] investigated the series $LaNi_{1-x}Co_xO_3$ in the temperature range of 80-320K. They obtained a RT figure of merit such as ZT=0.22 for x=0.8; that is directly comparable to that of $NaCo_2O_4$. This result was obtained by considering that the end members $LaNiO_3$ and $LaCoO_3$ are a strongly correlated n-type metal and a p-type insulator, respectively.

The end members $PrCoO_3$ and $PrNiO_3$ are n-type insulator ($S=-100\mu VK^{-1}$) [12] and n-type metal, respectively. In Figure 2, the S(T) curves for the $PrCo_{1-x}Ni_xO_3$ (x=0, 0.1, 0.2 and 0.3) samples are reported. The Ni^{2+} substitution for Co^{3+} induces a sign change of the TEP and also the largest Seebeck coefficient ($190\mu VK^{-1}$

at 300K). As the Ni^{2+} content is increasing, the S value is decreasing from $190\mu VK^{-1}$ to $58\mu VK^{-1}$ at RT. This observation is consistent with the increasing content of holes Co^{4+} in the Co^{3+} matrix. By considering the Heikes formula, we can extract the content of charge carrier per cobalt. We obtain 9%, 25% and 33% of Co^{4+} for $PrCo_{0.9}Ni_{0.1}O_3$, $PrCo_{0.8}Ni_{0.2}O_3$ and $PrCo_{0.7}Ni_{0.3}O_3$, respectively, which are close to the nominal content.

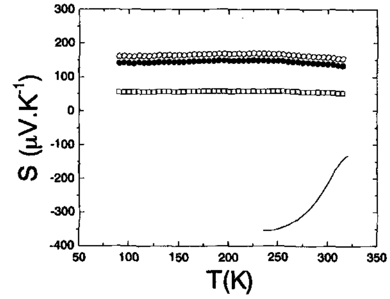

Figure 2: Seebeck coefficient versus temperature (T < 320K) curves for the $PrCo_{1-x}Ni_xO_3$ (x = 0 (straight line), 0.1 (open circles), 0.2 (closed circles) and 0.3 (open squares)).

By cationic substitutions, sign change can be induced either in hole or electron self-doped compounds.

The Brownmillerite $SrCoO_{3-\delta}$

Also, a similar S sign change is observed for $GdBaCo_2O_{5+\delta}$ series [11]. The Seebeck coefficient is negative for $\delta<0.5$ and positive for $\delta>0.5$. The sign change of S is induced for on each side of the +3 oxidation state, as in $LaCoO_3$ perovskite. We show here that this idea can be extended to another family, the brownmillerite compounds $SrCoO_{3-\delta}$. The synthesis procedure of $SrCoO_{2.5}$ is described in [13]. Figure 3 presents the thermopower and resistivity curves of $SrCoO_{2.5}$.

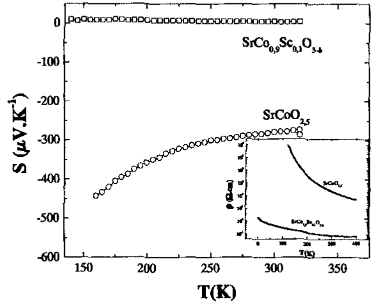

Figure 3: Thermopower and resistivity (Inset) versus temperature curves of the $SrCoO_{2.5}$ brownmillerite and $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ deficient perovskite.

A formal valency of Co^{3+} is expected in this material. The compound is insulating with a RT resistivity of 50 Ohm.cm. The thermopower is large and negative, close to $-280\mu VK^{-1}$ at RT. Its magnitude is decreasing with temperature as T increases. This negative sign shows that the cobalt valency is close to Co^{3+}, with a small amount of Co^{2+}. The insulating behavior reflects the presence of Co^{2+}/Co^{3+} as previously explained [14-15]. In order to stabilize a $SrCoO_{3-\delta}$ type phase, 10% of Sc^{3+} has been introduced on Co site, $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$. For this compound, S is positive with a very small value, $S_{300K}=4.1\mu VK^{-1}$. The transport is changed. In this case, the Co valence is far from +3 and thus the Heikes formula cannot be employed.

This composition might not be interesting for high temperature applications but it shows that the same idea as in cobalt perovskite can be applied in this brownmillerite structure.

Now, high temperature thermoelectric properties will be discussed.

III High temperature thermoelectric properties

$LaCoO_3$

In Figure 4, full range measurement of S has been reported for $LaCoO_3$ and $La_{0.99}Ce_{0.01}CoO_3$ compounds. The discontinuities in the curves at Figure 4 are due to change of measurement apparatus. Since the trivalent cobalt exhibits a thermally assisted spin-state transition around 500K from LS or IS toward HS state, as the temperature is increased, the absolute Seebeck coefficient value is decreased to reach a constant value near $18\mu VK^{-1}$ at 700K (Fig.4). The S value and sign become independent of the type of charge carriers, holes ($LaCoO_3$) or electrons ($La_{0.99}Ce_{0.01}CoO_3$).

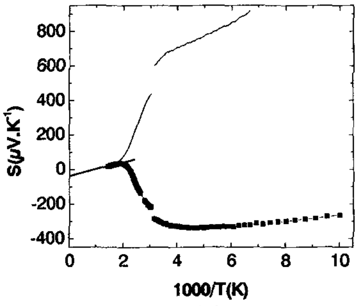

Figure 4: Seebeck coefficient versus temperature (50K<T<700K) curves for the $LaCoO_3$ (line) and $La_{0.99}Ce_{0.01}CoO_3$ (closed squares).

This behavior has been already observed by Kobayashi et al. [16] in the $CaM_{3-x}Cu_xMn_4O_{13}$ series and by Palstra et al. [17] in the $La_{1-x}Ca_xMnO_3$. In the transition-metal oxides, the thermopower in the high temperature limit is described by an extended Heikes formula $S = -(\frac{k_B}{e})\ln[\frac{g_3}{g_4}\frac{1-x}{x}]$, where g_i is the degeneracy of the electron configuration on the i ions and x is the concentration of the B cation. For the first authors, the S value at high temperature reaches $-25\mu VK^{-1}$ at 800-1000K. In these compounds, Mn^{3+} and Mn^{4+} cations are in the high spin state. Thus, the spin degeneracy correspond to g=2S+1 and should be equal to g_3=4 and g_4=5 for Mn^{3+} and Mn^{4+}, respectively. The equation can be written as $S=-(\frac{k_B}{e})\ln[\frac{4}{5}]-(\frac{k_B}{e})\ln[\frac{1-x}{x}]$. However, the value of the first constant term $S=-(\frac{k_B}{e})\ln[\frac{4}{5}]=-20\mu VK^{-1}$, corresponding to the experimental value obtained at high temperature. Similarly, neglecting the $[\frac{1-x}{x}]$ term, the same observation has been obtained by Palstra et al. [17] for the series $La_{1-x}Ca_xMnO_3$. The content of charge carriers does not influence the S value at high temperature. In the same way, in $LaCoO_3$ and derived compounds, different cations have to be considered: Co^{3+} HS (g=5) and Co^{2+} HS (g=4) or Co^{4+} (LS: g=2; IS: g = 4; HS: g = 6). Depending on the different combinations and neglecting the $[\frac{1-x}{x}]$ term, the calculated S constant values are in the range 77μVK^{-1} to -34μVK^{-1} in the high temperature limit. The experimental values, S~18μVK^{-1}, enter in this range. It confirms that S is independent of the concentration and the nature of charge carriers at high temperature but depends mainly on the spin degeneracy. Autret et al. [18] have also observed the same phenomena in the $LaMn_{1-x}Co_xO_3$ series where the S values of all the samples tend toward 30μVK^{-1} at 900K. The S constant value at high temperature has been attributed to the T activated dynamic disproportionation $2Co^{3+} \rightarrow Co^{2+} + Co^{4+}$. In this case, the experimental value reaches ~30μVK^{-1} at high temperature.

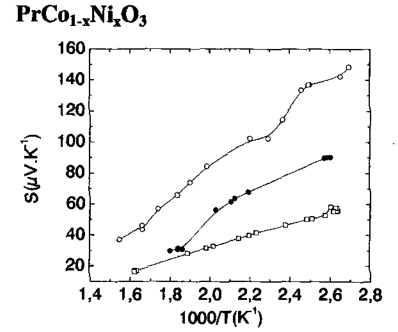

Figure 5: Seebeck coefficient (T > 320K) curve for the $PrCo_{1-x}Ni_xO_3$ (0.1 (open circles), 0.2 (closed circles) and 0.3 (open squares)).

As for $LaCoO_3$, when T increases beyond 300K, the S coefficient is decreasing for all the samples and the S values merge near 20-40μVK^{-1} (Figure 5) as reported by Yan et al. [11]. Co^{3+} cation in $PrCoO_3$ exhibits also a thermally assisted spin state transition around 500K towards high spin Co^{3+}. This transition could explain the continuous decrease of S with the increase of the temperature. Again, the TEP of these cobaltites tends to be independent of the charge carriers concentration at high temperature.

This result shows that there is a decoupling between the electrical percolation and the Seebeck percolation for the metallic $PrNiO_3$ phase. Taking into account the ρ and κ values of the $PrCo_{1-x}Ni_xO_3$ compounds, we have calculated the ZT values at 300K. The best value at RT is obtained for x=0.2. This value is higher than that reported for $NaCoO_2$ at 300K (ZT=0.03[13]). Such substitution is thus interesting to discover new TE materials.

Conclusions

In summary, we have studied the thermoelectric properties at low and high temperature of two perovskite $LaCoO_3$, hole self-doped, and $PrCoO_3$, electron self-doped. A sign change of S can be obtained by substituting the A- and B-site by tetravalent or divalent cations as illustrated by $LaCoO_3$ and $PrCoO_3$ perovskite, respectively. A good ZT value has been obtained for the compound $PrCo_{0.9}Ni_{0.1}O_3$ at 300K ZT=0.016. Nonetheless, due to the thermally cobalt spin state transition towards HS, the TE applications of these compounds are limited to T~RT. The existence of constant S values at high temperature show that the spin state degeneracy of the cobalt cations dominates and on the opposite that the charge carrier concentration plays a minor role. More studies of the high T physics of these cobaltites would have to be performed to understand these experimental results.

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