Search for New n-type Thermoelectric Oxides

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Abstract

The search for n type oxide thermoelements is very active as the thermoelectric performances of the n-type oxide legs are smaller than the ones of the p-type legs. Different strategies have been investigated in manganese and cobalt oxides to improve the figure of merit. First, by tuning the bandwidth of the manganese perovskites, the optimum of the power factor can be adjusted in temperature. The second part presents the results obtained in cobalt perovskites, where large p or n Seebeck coeeficients can be obtained by slightly doping $LaCoO_3$. This approach has then been applied to other families of cobalt oxides.

Introduction

The discovery of a large positive thermopower in the metallic oxide Na_xCoO_2 [1] has shown the great potentiality of oxides as thermoelectric materials for high temperature applications. Since then, numerous studies have been devoted to the investigation of the thermoelectric properties of different families of oxides. For thermogeneration applications, p-type and n-type materials with similar properties are needed and the search for large thermopower, positive or negative, is very active.

Among the different oxides families, the misfit cobalt oxides have been investigated in details. The structure of these compounds is built of similar CoO_2 layers as in Na_xCoO_2, separated by NaCl-like layers instead of Na [2]. These CoO_2 layers have been shown to be responsible for the large thermopower in these oxides [3], and the optimization of the thermoelectric properties of this family has thus been attempted.

The thermopower can be changed from +80μV/K (Tl/Sr/Co/O system [4]) to +170μV/K (Pb/Ca/Co/O system [5]) at room temperature depending on the NaCl-like separating layers. Despite all the different attempts, the thermopower always remains p-type and the variation of its amplitude remains rather limited. Potential n-type thermoelements have thus to be found in other structural families.

Previous promising results have been published in the ZnO and $ZnO\text{-}In_2O_3$ systems. The largest ZT of 0.33 at 1073K was reported in $(ZnO)_5In_2O_3$ at 1073K [6]. Other oxides are interesting. An all-oxide thermogenerator has been designed, using La doped $CaMnO_3$ as n-type leg [7]. More recently, Bi doped $LaNiO_3$ was used as a n type leg [8]. Despite all these studies, the thermoelectric properties of these n-type legs always remain below those of the p type leg [7].

We have previously investigated the thermoelectric properties of the electron doped manganese perovskites [9]. Starting from these results, the first part of the paper will present the results obtained for the optimization of the power factor S^2/ρ by tuning the bandwidth of these perovskites. The second part of this paper will show the possibility to get p and n type doped cobalt perovskites by carefully selecting the dopant oxidation state and the doping level. Following the Heikes formula [10], the thermopower and its sign depends on the nature of the charge carriers (electrons or holes), and starting from a stoichiometric compound, it is possible to get large positive or negative Seebeck coefficient, depending on the dopant. This idea has then been extended to other families of cobaltites.

Experimental

All the perovskites of the present study have been prepared by classical solid state reaction. The oxides precursors (for example : Co_3O_4, SrO_2, MnO_2,...) are intimately mixed in the stoichiometric proportions. The powder is compacted in the form of bars (typically 2×2×10mm) which are fired at high temperatures (1250°C for the perovskite cobaltites, 1400°C for the manganites).

The structures are 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 KEVEX analyser.

The transport properties have been measured using a Physical Properties Measurements System between 2K and 400K. The resistivity ρ is measured by the four probe technique with indium contacts deposited with ultrasonic waves. The thermopower S is measured by a steady-state technique.

Results

The $Ca_{1-x}Sr_xMn_{0.96}Mo_{0.04}O_3$ system

It has previously been shown that in manganese perovskites, electron doping can be an efficient way to design n type thermoelements. A and B site substitutions are effective in the $CaMnO_3$ compound, and a small fraction of Mn^{3+} can be introduced in the Mn^{4+} matrix, as for example in $CaMn_{1-x}Mo_xO_3$ or in $Ca_{1-x}Sm_xMnO_3$. This small electron concentration is responsible for the metallic behaviour and if the concentration is small, the thermopower absolute value remains large enough to be interesting for applications. For example, in $Ca_{0.95}Sm_{0.05}MnO_3$, S is close to −120μV/K at 300K and ρ~2mΩ.cm, which gives a Power Factor (PF) close to $7\mu WK^{-2}cm^{-1}$. Compared to the other conventional thermoelements, at RT this is still smaller than for example in Bi_2Te_3 ($40\mu WK^{-2}cm^{-1}$) [11].

The properties of these electron doped manganites can be described by a single band model [12]. We have tried to optimize the power factor following two ideas. First, by keeping the doping level constant, the thermopower should remain unchanged, at least at high temperature. Second, the bandwidth is known to be a crucial parameter in these materials and tuning the bandwidth should affect the electrical resistivity. This parameter can be modified by changing the size of the A site. We have therefore decided to investigate the $Ca_{1-x}Sr_xMn_{0.96}Mo_{0.04}O_3$ system.

The structural study reveals a complex phase diagram with two structural transitions observed from orthorhombic to quadratic for x~0.3 and quadratic to cubic for x~0.8 [13]. Furthermore, as the Sr content increases, the antiferromagnetism is reinforced because of the modification of the Mn-O-Mn angle [14].

Figure 1 presents the results obtained for the resistivity.

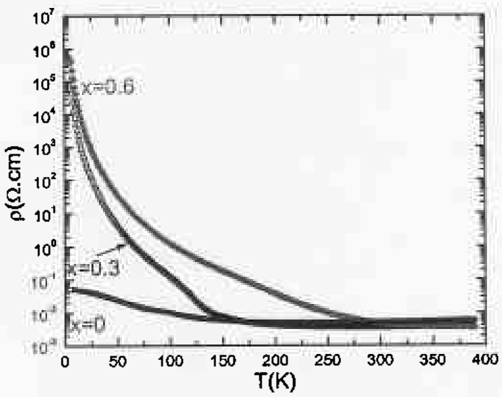

Figure 1: ρ(T) of the $Ca_{1-x}Sr_xMn_{0.96}Mo_{0.04}O_3$ system

The Sr substitution induces a strong localization at low T and as x increases, the metallicity is progressively destroyed. For x=0.6, the sample resistivity presents a dρ/dT<0 in the whole range of temperature. The most interesting point is that the value of ρ remains almost unchanged at RT, close to 4mΩ.cm, and that ρ decreases as T increases for x>0.4. The increase of resistivity is associated to the strengthening of the antiferromagnetic interactions.

Figure 2 presents the results obtained for the thermopower. The low T thermopower is strongly affected by the Sr substitution. For this electron doped system, the Seebeck coefficient evolves from negative to positive at low T, depending on the magnetic interactions [13]. However, at high T, i.e. above 250K, all the curves merge onto a single one, with a linear variation of S as T increases : S is close to –100μV/K at 300K and its magnitude increases as T increases. The close values of S obtained for all the samples shows that S is mainly determined by the valency, constant here, at RT, as expected from the Heikes formula [10].

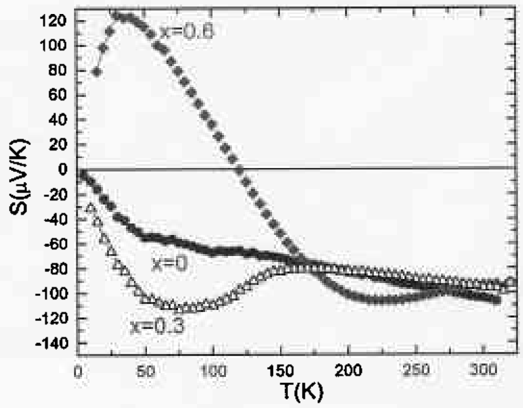

Figure 2: S(T) of the $Ca_{1-x}Sr_xMn_{0.96}Mo_{0.04}O_3$ system

Combining the S(T) and ρ(T) curves, the Power Factor can be calculated and is presented in figure 3.

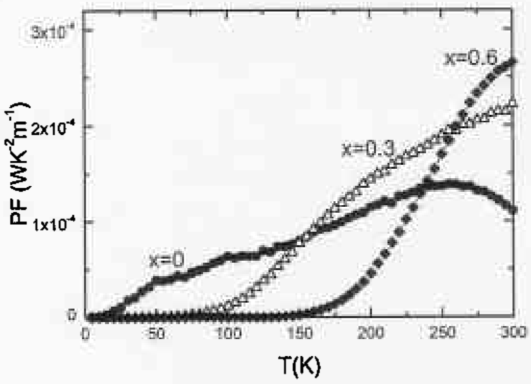

Figure 3 : PF=S^2/ρ of the $Ca_{1-x}Sr_xMn_{0.96}Mo_{0.04}O_3$ system

The Sr for Ca substitution is an efficient way to increase the Power Factor in these materials. The beneficial effect is mainly coming from the change in ρ(T) observed in figure 1. First, there is a very small decrease of ρ at RT for the larger x content which induces an increase of PF. Second, the most interesting point is that the variation of PF with T is affected and its maximum is shifted to higher temperature as x increases. In figure 3, even if the absolute value of the Power Factor is not maximized, it is clear that the maximum of PF(T) can be adjusted in temperature, by tuning the bandwidth in these perovskites.

p and n type thermoelements in the $LaCoO_3$ system

The high temperature thermopower can be estimated from the Heikes formula [10].

$$S = \frac{k_B}{e}\ln\left(\frac{1-x}{x}\right)$$, where x is the carrier concentration.

For a small x, S can reach very large values. Starting from the stoichiometric perovskite $LaCoO_3$, it should be possible to keep a large S for a small x, with S positive or negative depending on the nature of the dopant [15]. The transport properties of the A or B site substituted $LaCoO_3$ have been investigated. Doping with Sr^{2+} should induce a Co^{3+}/Co^{4+} mixed valency, i. e. a p type doping whereas doping with Ti^{4+}, Sn^{4+} or Ce^{4+} induces a Co^{2+}/Co^{3+} mixed valency, i. e. a n type thermoelement.

Figure 4 presents the resistivity curves of these compounds. All the samples are insulating, with ρ~0.1–10Ω.cm at RT. The Sr compound shows a spectacular decrease of resistivity in the whole T range.

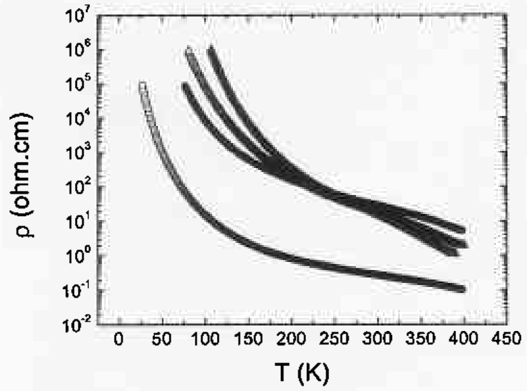

Figure 4 : T dependence of resistivity for $LaCoO_3$ (closed triangles), $La_{0.98}Sr_{0.02}CoO_3$ (open circles), $La_{0.99}Ce_{0.01}CoO_3$ (closed circles), $LaCo_{0.99}Ti_{0.01}O_3$ (open triangles).

This strong asymmetry might be related to the different kinds of carriers, holes or electrons responsible for the conductivity. The thermopower measurements is a direct probe of the sign of carriers.

Figure 5 presents the thermopower of the different samples investigated here. The measurements are restricted to the resistance values smaller than 10^5Ω.

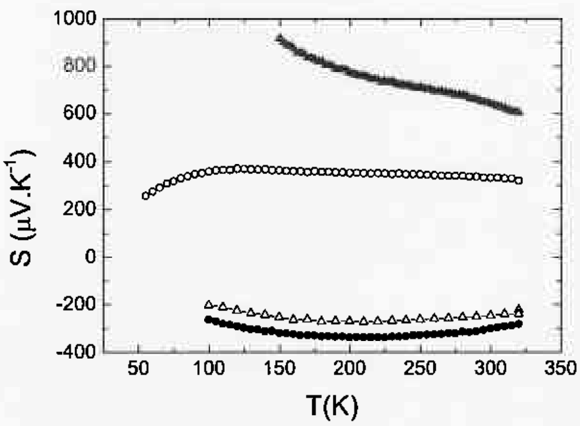

Figure 5 : S(T) for $LaCoO_3$ (closed triangles), $La_{0.98}Sr_{0.02}CoO_3$ (open circles), $La_{0.99}Ce_{0.01}CoO_3$ (closed circles), $LaTi_{0.01}Co_{0.99}O_3$ (open triangles).

The parent compound $LaCoO_3$ exhibits a very large, positive Seebeck coefficient of +600µV/K at RT. The positive value reflects that the sample is slightly self-doped with holes, but that the self-doping remains very small as S is very large. The Sr substitution induces a strong decrease of S, with S close to +300µV/K at RT. This is consistent with the increase of Co^{4+} induced by the Sr^{2+} substitution : only 2% of Co^{4+} reduces S from +600 to +300µV/K.

Figure 5 shows that a spectacular sign change can be obtained in these perovskites when they are doped with tetravalent cations, on the A (Ce) or B(Ti) sites. With only 1% of Co^{2+}, S sign changes and reaches –300µV/K at RT.

Even if the thermopower values can be symmetric (+300µV/K or –300µV/K), the resistivity data are different, with a smaller ρ in the p type cobaltites. This is due to the fact that the transport takes place in the t_{2g} band of the 3d orbitals for Co^{3+}/Co^{4+} and in the e_g band for Co^{2+}/Co^{3+}.

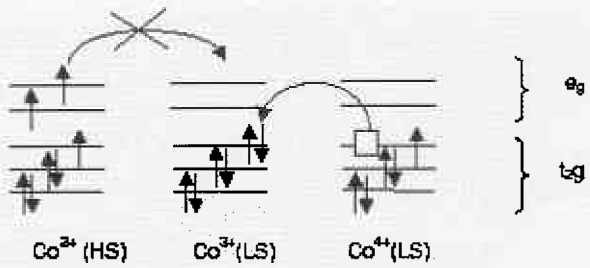

Figure 6 : Schematic description of the hopping of Co^{2+} or Co^{4+} in a Low spin Co^{3+} matrix.

The transport is easier in the t_{2g} band than in the e_g one [16] because a conduction band can be formed in the t_{2g} band just by interchanging a Low Spin Co^{3+} and a Low Spin Co^{4+} by moving only one spin ½. On the other hand, with a High Spin Co^{2+}, the hopping in the e_g band is not possible by moving only one electron.

Figure 7 summarizes the values of S at RT obtained in the different substituted samples as a function of the carrier concentration. The solid line represents the values calculated from the Heikes formula.

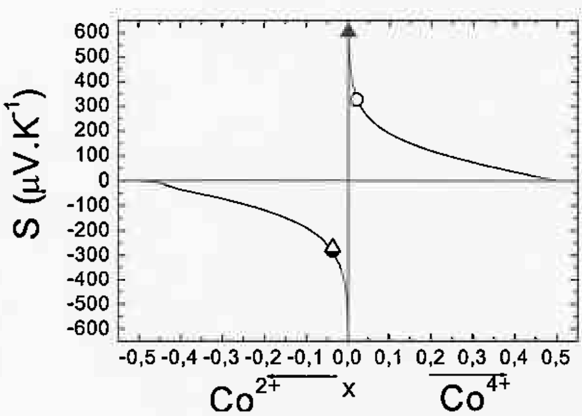

Figure 7: Theoretical S(x) curves from the Heikes formula. The experimental points for $LaCoO_3$ (closed triangles), $La_{0.98}Sr_{0.02}CoO_3$ (open circles), $La_{0.99}Ce_{0.01}CoO_3$ (closed circles), $LaTi_{0.01}Co_{0.99}O_3$ (open triangles) are shown with the same symbols as the S(T) curves.

The experimental data are in good agreement with the calculated values. This plot demonstrates that by carefully choosing the dopant, and by making only very small substitutions, p and n type thermoelements can be generated in the same family of oxides. This is important especially for devices where thermoelements of both types, with similar thermoelectric and mechanical properties are required.

The Brownmillerite $SrCoO_{3-\delta}$

The possibility to change the sign of the Seebeck coefficient has been shown also in the $GdBaCo_2O_{5+\delta}$ family [17]. 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 [18]. Figure 7 presents the thermopower and resistivity curves ofSrCoO$_{2.5}$.

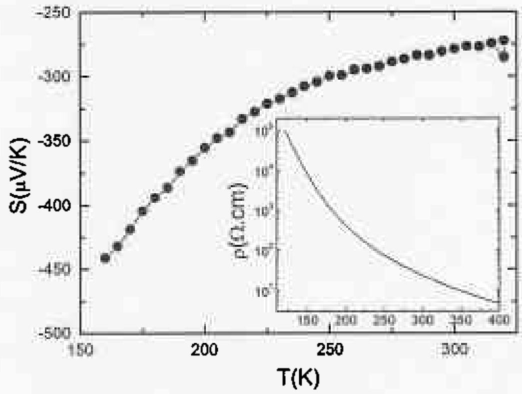

Figure 7 : Thermopower and Resistivity (Inset) versus temperature of the $SrCoO_{2.5}$ brownmillerite

A formal valency of Co^{3+} is expected in this material. The compound is insulating with a RT resistivity of 5 Ω.cm. The thermopower is large and negative, close to $-280\mu V/K$ 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 [15-16]. This composition might not be interesting for high temperature applications but it shows that the same idea as in cobalt perovskites can be applied in this brownmillerite structure.

Conclusion

The thermoelectric properties of n type oxides have been investigated. By tuning the bandwidth in manganese perovksites, we have shown that the power factor maximum can be adjusted in temperature. The second parameter which has been investigated is the doping level and its nature. Following the Heikes formula, it is shown that starting from the $LaCoO_3$ perovskite, a light doping can induce p or n type thermoelements with a large thermopower. The resistivity values are nevertheless not symmetric, as the transport is easier in the hole doped systems than in the electron ones. The efficiency of p type or n type doping can be extended to other families, such as the brownmillerite. These three different examples show the richness of the oxides family. The optimization of the thermoelectric properties is not achieved yet, and the other major task is now to investigate the high temperature properties of these promising oxides.

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