LARGE THERMOPOWER IN METALLIC OXIDES:
MISFIT COBALTITES AND MANGANO-RUTHENATES

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ABSTRACT

Two different kinds of metal transition oxides have been studied for their large thermopower values. The first one corresponds to the Tl-based misfit cobaltite which is a hole-doped metal. We demonstrate that the partial Bi-substitution for Tl in this phase induces an increase of the room temperature (RT) thermopower (TEP) value. Same result is obtained with the new Pb1/3SrCoO3+δ misfit corresponding to the Tl complete replacement by lead. Simultaneously, the T dependence of their resistivity exhibits a re-entrance below 70-90K where a large negative magnetoresistance is observed. Magnetic measurements reveal a strong interplay between spins and charges for this class of materials.

Electron-doped (n-type) perovskite manganites are a second class of potential candidates for applications. In particular, the Ru4+/5+ substitution for Mn in the CaMnO3 semi-conductor induces a drastic drop of the resistivity values. Metals with large RT TEP values and not too large thermal conductivities are generated. A comparison with best known materials, Bi2Te3 and NaCo2O4 is made.

1. INTRODUCTION

Metal transition oxides exhibit various kinds of spectacular physical properties such as high Tc superconductivity (HTCS) in cuprates and colossal magneto-resistance in manganites. More recently, Terasaki et al [1] have shown that the NaCo2O4 cobaltite exhibits a high figure of merit Z and since then the research for new metallic oxides with large thermopower (TEP) values to be used for applications to convert heat in energy has become a 1g and two e’ g orbitals with light and heavy holes, respectively [8]. These CoO2 layers are metallic and they are thought to be responsible for the large thermopower TEP values. In contrast, the array of corner-shared CoO6 octahedra in the La1-xSrCoO3 perovskite exhibits only small TEP values when the CoO4+ concentration becomes sufficient to reach metallicity [9].

The structural difference between NaCo2O4 and misfit cobaltites lies thus in the separating layer, randomly half-filled Na layers and rock-salt type layers for the former and the latter are described in parts 2 and 3, respectively.

2. MISFIT COBALTITES

The structures of the NaCo2O4 [7] and the misfit cobaltites contain the same type of CoO2 layers. The edge-shared CoO6 octahedra form a layer of triangular cobalt in which the trivalent and tetravalent cobalt cations remain in the t2g and t2g low-spin state, respectively. The rhombohedral crystal field splits further the t2g orbitals in one a2g and two e’ g orbitals with light and heavy holes, respectively [8]. These CoO2 layers are metallic and they are thought to be responsible for the large thermopower TEP values. In contrast, the array of corner-shared CoO6 octahedra in the La1-xSrCoO3 perovskite exhibits only small TEP values when the CoO4+ concentration becomes sufficient to reach metallicity [9].

Among these misfit cobaltites, there exist two types of phases which differ by their c cell parameters (the c direction corresponds to the layer stacking). This reflects their different number of separating layers: c ~ 11Å and c ~ 15Å for 3 and 4 layers, respectively. The latter corresponds to the [Bi1.82SrO2]1.62[CoO2]1.82 [5] misfit oxide and derived phases in which Pb replaces partially Bi. Their TEP properties have already been extensively reported see for instance ref. [10]. The other class of misfits corresponds to the Tl-based, Tl[CoO]1.62[CoO2] [4, 12], and CaCo-based [CoO2:CaO1.5-x][CoO2]1.62 [11]
phases, also written for sake of clarity $\text{Tl}_2\text{SrCoO}_3$+$\delta$ and $\text{Ca}_3\text{Co}_4\text{O}_9$.

In the following we will focus on the Tl-based misfit cobaltite.

### 2.1 BISMUTH SUBSTITUTIONS FOR THALLIUM

Structural similarities between the RS type layers of misfit cobaltites and of HTCS have opened the route to the discovery of new Tl-based misfit cobaltites. Because bismuth and lead were substituted for Tl in the case of Tl-based cuprates such as the Tl$\text{Sr}_2\text{CaCu}_2\text{O}_7$ “1212” superconductor leading to the following formulae, Tl$^{\frac{2}{3}}$Bi$^{\frac{1}{3}}$Sr$^2$CaCu$^2$O$_7$ and Tl$^{\frac{1}{2}}$Pb$^{\frac{1}{2}}$Sr$^2$CaCu$^2$O$_7$, several attempts of Bi or Pb substitutions for Tl have been made in the Tl-based misfit prepared in silica tubes with a one-step method [4].

In the case of the bismuth substitution, it is found that a single misfit phase of analyzed cationic composition “Tl$^{0.28}$Bi$^{0.14}$SrCo” can be stabilized by starting from the nominal composition (Tl$^{\frac{2}{3}}$Bi$^{\frac{1}{3}}$)$^{0.6}$SrCoO$_{4.28}$. It should be pointed out that by starting from the Tl/Bi = 1 ratio, a Tl/Bi = 2 final ratio is always measured by EDS, indicating the great stability of the phase corresponding to the ratio Tl/Bi = 2 as it is the case for the Tl$^{\frac{2}{3}}$Bi$^{\frac{1}{3}}$-1212 superconducting cuprate.

![Fig. 1: ρ(T) curves of Tl$^{0.28}$Bi$^{0.14}$SrCoO$_{3+\delta}$ ("TlBi") and Tl$^{2/3}$SrCoO$_{3+\delta}$ ("Tl"). Tl and Bi contents are the results of EDS analyses.](image)

Although the Bi for Tl partial substitution does not modify significantly the 300 K resistivity value, $\rho_{\text{TlBi}} = 20$ mΩ.cm against $\rho_{\text{Tl}} = 12$ mΩ.cm for the more conductive sample (see the corresponding ρ(T) curves in Fig. 1), the low-T part of the curve is dramatically changed by the Bi substitution which induces a semi-conducting like re-entrant behavior below 60 K. Accordingly, $\rho$ reaches a minimum value of 10 mΩ.cm at 60 K and then increases as T further decreases to reach $\rho = 38$ mΩ.cm at 5 K. A similar $\rho$ (T) shape was also found in the case of the Ca$_3$Co$_4$O$_9$ misfit [11] in the form of polycrystals or single-crystals (along the ab-plane). This shape modification of the ρ (T) curve compared with that of the Tl-Sr-Co-O misfits can be ascribed to the different magnetic behavior induced by Bi. As shown in the T dependent inverse susceptibility $\chi^{-1}$(T) curves of Fig. 2, the TlBi misfit undergoes a magnetic transition below 10 K and $\chi^{-1}$ starts to deviate from the linearity below ~ 50 K, whereas the Tl-Sr-Co-O misfit remains paramagnetic down to 2K.

![Fig. 2: T dependent inverse magnetic susceptibility ($\chi^{-1}$) of "Tl" and "TlBi" misfits. $\chi^{-1}$ values are calculated from magnetization data measured with a SQUID magnetometer ($\mu_0H = 0.3$T).](image)

This is also shown in Fig. 3 where a clear hysteresis is found in the M(H) loop of the Tl/Bi misfit. Accordingly, in the absence of applied magnetic field, disorder in the spins alignment make that the resistivity increases as the sample becomes magnetic and under field application, the spin scattering reduction leads to a negative magnetoresistance (MR). If one defines MR as $MR = -100 \times [\rho_H/\rho_{H=0} - 1]$, MR reaches 25 % in 7T at 2K for TlBi, whereas, in the absence of magnetic ordering, the magnetoresistance is positive in the Tl misfit reaching only 2% in 7T which is characteristic of a metal.

Interestingly, the thermopower values (Seebeck, S) of the TlBi-misfit are larger than those of the Tl-misfit (see Fig. 4), +120μV.K⁻¹ and +90μV.K⁻¹ at 300K for TlBi and Tl based misfit, respectively. In fact, the TlBi $S_{300K}$ value is similar to that of Ca$_3$Co$_4$O$_9$ as also shown on this figure.
2.2. LEAD SUBSTITUTION: Pb_{1/3}SrCoO_{3-δ} A NEW MISFIT COBALTITE

Similarly to the Bi substitution, we have tried to replace partially Tl by Pb. First of all, by varying the nominal Pb content from x = 0.1 to x = 0.3 in Tl_{0.6-\delta}Pb_{0.4}SrCoO_{4.28}, the EDS analyses of the reacted materials always reveal the existence of a phase mixture made of a Pb rich and a Pb poor misfit cobaltites, contrasting with the aforementioned Bi substitution. This result could be possibly due to the higher thermodynamical stability of the end members –pure Tl and pure Pb misfit- compared to the mixed Tl/Pb-misfit.

This has motivated us to try the synthesis of a pure Pb misfit cobaltite by using the following experimental: stoichiometric amounts of oxides and peroxides, PbO₂, SrO₂, Co₃O₄ are mixed and pressed in the form of bars. The latter are sealed under vacuum in silica tubes with approximately 0.8g of bars for a volume of 3cm³ in the tube. Then, the tubes are heated in 6h at 900°C for 12h and finally cooled down to RT in 6h. After the reaction completion, black ceramic bars are obtained.

Best samples quality is achieved by starting from Pb₈SrCoO₁₃ which yields cationic compositions ‘Pb₁/₃SrCo’ after reaction.

The structure of this misfit [13] is isostructural to that of Tl₈SrCoO₃-δ and Ca₃Co₃O₆, i.e. three layers [SrO]-[(PbSr)O]-[SrO] are interleaved with the [CoO₂] layer.

One interesting property of the Tl-, Bi/Pb- and Ca-based misfit cobaltite lies in their large thermopower (S) at room temperature, always in the range 90µV.K⁻¹ to 130µV.K⁻¹, which is similar to S_{00K} = +100µV.K⁻¹ reported for NaCo₂O₄ [1]. From all these thermopower results, it is tempting to associate the large S value with the peculiar CoO₂ layer common to all these oxides. The thermopower values obtained for the pure lead misfit cobaltite reinforce this hypothesis. As shown in Fig. 5, at RT the value for the Pb/Sr/Co/O misfit is found to be close to +110µV.K⁻¹. This value is also close to that exhibited by (Tl/Bi)₈SrCoO₃-δ in Fig. 4. And similarly, the resistivity at low T exhibits also a re-entrance (Fig. 5). The T dependent ρ curve exhibits thus a ρ minimum at about T_min = 90K for the pure Pb cobaltites.

The physical properties of these new Pb misfit cobaltite are also very like that of Ca₃Co₃O₆ which exhibits same kind of S(T) and ρ(T) characteristics. A negative MR is also found in Ca₃Co₃O₆.

2.3. CONCLUSIONS

Among the misfit cobaltites, the Tl/Sr/Co/O one is unique since this is the only compound which exhibits metallicity and paramagnetism down to the lowest temperature accompanied by a positive magnetoresistance [12]. As discussed in the paper by Singh on the electronic structure of NaCo₂O₄ [8], it is very difficult to predict the low T magnetic state of the cobalt oxides made of CdI₂-type CoO₂ layers since magnetically ordered or paramagnetic solutions cannot be distinguished. In this respect, the chemical route consisting in the Bi for Tl substitution is interesting since on the one hand, it induces at low T, a re-entrant resistivity and negative magnetoresistance, and, on the other hand, an increase of the thermopower value at RT. In this respect, the new Pb/Sr/Co/O misfit behaves more like the Tl/Bi-misfit cobaltite than the pure Tl one. It should be pointed out that in these cobaltites, all the compounds exhibiting a RT thermopower value larger than that of Tl-based misfit show a negative magnetoresistance linked to the re-entrance in the resistivity at low T. This demonstrate the existence of the interplay between charges and spins in this class of oxides.

Since all the thermopower values of misfit cobaltites are close to those of NaCo₂O₄, one has to consider that the peculiar rhomboedral splitting of the a₁g orbitals of Co³⁺/Co⁴⁺ of the CoO₂ layer into a₁g and e′,g levels is responsible for these high values. In this framework, it was proposed that the narrow band made of heavy holes in the a₁g orbitals mostly contributes at the Fermi level to yield large thermopower [8]. It appears thus that this band is not very sensitive to the nature of the separating layers interleaved between the CoO₂ layer. In contrast, the different behaviors of resistivity and magnetism can be interpreted as the result of a modification in the filling or in the position of the e′,g band made of mobile holes. However, the composite nature of these misfit oxides makes very difficult the refinements of their structures. Subtle changes in the cell parameters can affect the a₁g and e′,g respective contributions at E_F. Single-crystals are now required to quantify the mobile holes density by Hall effect and to check simultaneously the structural changes.
induced by Bi for Ti partial substitution or the complete replacement of Ti by Hg. Thermal conductivity measurements are also required to compare the figures of merit of these different misfit cobaltites to that of NaCo$_2$O$_4$.

3. MANGANESE OXIDES

3.1 CMR PROPERTIES

Manganese oxides have been the subject of a renewed attention in the last few years after the discovery of Colossal Magneto Resistance (CMR) [for recent reviews see ref. 14].

Manganites crystallize in the perovskite structure. It can be described as a cubic close packed array with O anions at the centers of the faces, the lanthanide and alkaline rare-earth (La, Pr, Ca, Sr…) at the corner (site A) and Mn ion at the center in the octahedral interstitial site (site B). The ideal cubic structure is strongly distorted due to the cation size mismatch and due to the Jahn-Teller effect active for Mn$^{3+}$.

The parent compounds (for example, LaMnO$_3$ with a manganese valency equal to 3 or CaMnO$_3$ with only Mn$^{4+}$) are anti-ferromagnetic insulators. The Mn$^{3+}$ and Mn$^{4+}$ electronic structures are respectively 3d$^4$ and 3d$^3$, which following Hund’s rule correspond to orbital filling $t_{2g}$, $e_g$, and $t_{2g}^6$. When doping the A site with a divalent cation (for LaMnO$_3$) or trivalent cation (for CaMnO$_3$), mixed valent manganese is introduced and CMR properties can appear. They are linked to the appearance of ferromagnetism in these materials, usually simultaneously occurring with a metal/insulator transition separating the high temperature paramagnetic insulating phase from the ferromagnetic metallic low temperature phase. For the optimal composition corresponding to 30% of Mn$^{3+}$, a huge magnetoresistance is observed as for example in Pr$_{0.7}$Ca$_{0.26}$Sr$_{0.04}$MnO$_3$ [15] where the resistance drops by more than 11 orders of magnitude when applying 5T.

A first attempt to explain the CMR properties is based on the double-exchange model [16]. In such a model, the hopping integral of the $e_g$ electron is proportional to the angle between the manganese ions Mn$^{3+}$/Mn$^{4+}$. When applying a magnetic field, the alignment between manganese ions is favored and the resistivity decreases, leading to negative magneto-resistance. It was however shown that double-exchange model can qualitatively but not quantitatively explain CMR [17] and several studies have revealed the importance of electron-phonon interactions to understand these phenomena. These manganites are actually a nice framework to investigate the interplay between spins, phonons and carriers.

As CMR is more important for the hole doped manganites than for the electron doped ones, most of the studies have focused on this doping side, with investigation of the A site or B site doping to try to optimize CMR and to understand its origin. More recently, it was found that CMR can also be found in electron doped manganites such as Ca$_{1-x}$Sm$_x$MnO$_3$ with x<0.15[18].

In both cases (electron or hole doped manganites) thermoelectric properties, as other transport and magnetic properties, are dramatically modified by doping. The undoped insulating compounds have in both cases large thermopower and high resistivity ; for example at room temperature, $S=-350 \mu$V/K and $\rho=2\Omega$cm for CaMnO$_3$, and $S=+450 \mu$V/K and $\rho=10\Omega$cm for LaMnO$_3$. With doping, thermopower decreases as holes or electrons are introduced. Simultaneously resistivity is decreased and because of the lower concentration of Mn$^{3+}$ Jahn-Teller cations for the electron side, resistivity can be as low as 1m$\Omega$cm (see [6]), much smaller than the values typically of the order of a few $\Omega$cm obtained for doped LaMnO$_3$.

3.2 A SITE DOPING OF CaMnO$_3$

Results concerning the series Ca$_{1-x}$Sm$_x$MnO$_3$ (x<0.12) are presented on Fig. 6.

Fig. 6 : a) M(T) curves measured under an applied field of 1.45T for Ca$_{1-x}$Sm$_x$MnO$_3$.

b) $\rho$(T) curves measured under zero applied field

The magnetization (fig. 6a) was measured under 1.45T after zero field cooling as a function of temperature. The substitution of Ca by Sm leads to ferromagnetic interactions but the magnetic moment remains smaller than...
As $x$ increases, the metallicity increases which induces a decrease of the absolute value of thermopower. The values of $S$ at 300K remain nevertheless large for metals (for example, $-120 \mu V/K$ for $x=0.05$). Thermopower is negative in the whole temperature range with a linear temperature dependence in the paramagnetic region. Below $T_c$, an increase of $|S|$ (for $x=0.05$ and $x=0$) or a decrease (for $x=0.1$) associated with the onset of magnetic ordering is observed, then the thermopower decreases to very small values as $T$ tends to 0. $S$ can be described by a single band metal model with

$$S = \pi^2 k_B^2 / 3e k_B T \partial \ln \sigma(E) / \partial E.$$  

Using the values of $S$ and $\sigma$ at 300K, the number of carriers $n(E)$ (with $\sigma(E)=n(E)\times e\times \mu(E)$, where $\mu(E)$ is the carrier mobility) can be extracted and is found to be very close to the values expected from chemical formula (see [6]) with typically $N(E)/n(E)$ close to 7-12 depending on $x$ (with $N(E)$ the density of states).

Combining $S$ and $\rho$ values at room temperature, the power factor $P=S^2/\rho$ is equal to $7\mu W K^{-2} cm^{-1}$ for $x=0.05$, a value very large compared to other oxides (except $NaCo_2O_4$ and cobalt misfits) and only 4 times smaller than the power factor of $Bi_2Te_3$ [1]. This value is still smaller than the best reported power factor obtained in single crystals of $NaCo_2O_4$ of $50\mu W K^{-2} cm^{-1}$ [1]. Note however that the properties reported here concern polycrystalline samples for which conductivity could be improved and thus increase power factor. In the case of $NaCo_2O_4$ there is indeed a large difference between the power factor of crystals ($50\mu W K^{-2} cm^{-1}$ [1]) and the one of polycrystalline samples ($2\mu W K^{-2} cm^{-1}$ [20]).

To calculate the figure of merit $Z = S^2/(\rho\kappa)$, thermal conductivity measurements have been carried out. Figure 8 presents the results obtained for the same compounds as those of Figure 7.

The thermal conductivity is small for these metallic oxides (maximum $7 W m^{-1} K^{-1}$), but still much larger than for $NaCo_2O_4$ for which a value of $2 W m^{-1} K^{-1}$ was reported at room temperature [20]. This relatively large value is not favorable to get large $Z$. A reasonably small value of $\kappa$ can be reached only for large $x$ but as increasing $x$ in $Ca_{1-x}Sm_xMnO_3$ would only decrease $S$ and increase $\rho$ [21], another route to improve thermoelectric properties has been investigated.

### 3.3 Mn SITE DOPING IN CaMnO$_3$

Several cations have been investigated as possible dopants on the B site of CaMnO$_3$. First studies were dedicated to the investigation of CMR properties and the idea was to substitute Mn by a cation with a valency superior to 4 to induce mixed valency Mn$^{3+}$/Mn$^{4+}$ and thus favor CMR properties.
Using non magnetic cations $d^0$ (Nb, Ta, W and Mo) as substitution cation $M$ in $\text{CaMn}_{1-x}\text{M}_x\text{O}_3$, it was indeed found that CMR appears for $x$ as small as 0.02 [19]. This is due only to a valency effect which favors the appearance of mixed valency together with double-exchange interactions, and disappears for tetravalent cations such as $\text{Ti}^{4+}$.

To further improve CMR, more attention has been paid to Ru because of its possible mixed valent state Ru$^{4+}$/Ru$^{5+}$ with isoelectronic structure of Mn$^{3+}$/Mn$^{4+}$ ($d^4$ and $d^3$) which could enhance ferromagnetic interactions by superexchange coupling between Ru and Mn.

Figure 9 represents the magnetization as a function of temperature measured under 1.45T after zero-field cooling for $\text{CaMn}_{1-x}\text{Ru}_x\text{O}_3$ ($0 \leq x \leq 0.5$).

In a similar manner as in $\text{Ca}_{1-x}\text{Sm}_x\text{MnO}_3$, magnetic moment continuously increases when $x$ increases, reaching $0.8\mu_B$ for $x=0.4$ and then decreases again for $x>0.4$. Ferromagnetism is induced by Ru doping but the magnetic moment remains very small compared to the expected moment as for A site doping. This reveals a non uniform material with phase separation phenomena: at room temperature, the material is structurally single-phase (orthorhombic), but at low temperatures, high resolution electronic microscopy performed at $T=92K$ reveals the existence of an antiferromagnetic distorted phase coexisting with ferromagnetic orthorhombic regions. Most interestingly, this phase separation phenomenon leads to a large increase of magneto-resistance [22].

Resistivity measurements are presented in Fig. 10. $\rho$ continuously decreases as $x$ increases up to $x=0.12$. For larger $x$, the room temperature resistivity increases while the low temperature values remain small. For a thermoelectric use close to room temperature, the range of possible $x$ is therefore limited to $x<0.2$. A minimum value of $\rho=2m\Omega\cdot cm$ is obtained at 300K for $x=0.12$. As for the series $\text{Ca}_{1-x}\text{Sm}_x\text{MnO}_3$, these data can be fit by the small polaron model, but contrary to this case, the hopping energy decreases as $x$ increases (from 37.5meV for $x=0.06$ to 28.4 meV for $x=0.1$) [23].

Compared to the other non magnetic cations previously used (Nb, Mo…), $\rho^{300K}$ is smaller in the case of Ru than in the case of non magnetic cation. For example, for Nb, a minimum value of 8 m$\Omega$·cm is obtained for 6% of Nb. In the case of non magnetic cations, even if ferromagnetism is induced and favors metallicity, the presence of foreign cations on the B site disturbs the hopping transport of electrons along the Mn network. On the other hand, for Ru, ferromagnetic interactions and thus metallicity are enhanced because of superexchange interactions between Mn and Ru and furthermore, the $e_g$ electron of Ru$^{4+}$ can participate in the transport phenomena, reducing the 'electronic disorder' on the Mn network [24].

Thermoelectric properties of the Ru doped $\text{CaMnO}_3$ are presented in Fig. 11. As metallicity is enhanced when Ru is introduced, the TEP $S$ is decreased in the whole temperature range compared to the undoped compound $\text{CaMnO}_3$. For a $x$ value which corresponds to reasonably small values of $\rho$ (5m$\Omega$·cm for $x=0.06$), $S$ at 300K is decreased but remains very large close to -140$\mu$V/K.

Larger values of $x$ induce a strong decrease of $S$ together with a strong increase of $\rho$.

Ru is a unique dopant for $\text{CaMnO}_3$ as its electronic structure similar to that of Mn favors the interactions...
between Mn and Ru and reinforces metallicity. Furthermore, the other advantage, compared to other dopants, is that because of its mixed valency (between 4 and 5), it decreases the Mn valency less rapidly than other pentavalent or hexavalent cations. S is very sensitive at high temperatures to the carrier concentration and following Heikes formula, decreases as the Mn valency decreases. The slow decrease of Mn valency induced by Ru thus preserves large values of S compared to other dopants. This is illustrated in Fig. 12.

![Fig. 12: S(T) of CaMn$_{0.94}$M$_{0.06}$O$_3$](image)

Except for tetravalent Sn$^{4+}$ (which does not induce metallicity), S is strongly reduced by the substitution of 6% of foreign cation. However, the reduction is less drastic for Ru than for Nb or Re, both pentavalent cations. At room temperatures, even if the three compounds have similar resistivity, the power factor will be larger for Ru.

Figure 13 presents the thermal conductivity of the same compounds as in Fig. 12.

![Fig. 13: $\kappa$(T) of CaMn$_{0.94}$M$_{0.06}$O$_3$](image)

Thermal conductivity is rather small as for Ca$_{1-x}$Sm$_x$MnO$_3$ but the reduction of $\kappa$ at room temperature is more important than for the A site doping. $\kappa$ remains smaller than 5 Wm$^{-1}$K$^{-1}$ for 6% of Ru. Considering the Lorenz number $L=\kappa/\sigma T = 2.44 \times 10^{-8}$ WΩK$^{-2}$, the estimated electronic contribution to $\kappa$ is close to 0.24 Wm$^{-1}$K$^{-1}$ at room temperature in the case of Ru, showing that $\kappa$ is dominated by the phonon contribution. Combining $\rho$, S and $\kappa$, we obtain a figure of merit equal to 1.33 $10^{-4}$ K$^{-1}$ at 300K which makes it as good as the best thermoelectric oxide NaCo$_2$O$_4$.

The stronger reduction of $\kappa$ in the case of B site doping compared to Ca$_{1-x}$Sm$_x$MnO$_3$ is linked most probably to the fact that disorder on the B site is detrimental for the heat propagation as carriers and phonons are strongly coupled, as evidenced by the small polaron behavior of resistivity.

### 3.4 CONCLUSIONS

Table 1 summarizes the results obtained at room temperature with manganese oxides and compare them to the other best thermoelectric oxides and to ‘standard’ thermoelectric materials.

| Compound | $\rho$ (mΩcm) | $\kappa$ (Wm$^{-1}$K$^{-1}$) | $\rho S$ ($\mu$WK$^{-1}$cm$^{-1}$) | $ZT$ at 300K |
|----------|----------------|-----------------|-----------------|---------------|
| Ru doped CaMn$_x$O$_3$ ($x=0.06$) | 2 | 4 | 0.032 | 0.030 |
| Sm doped CaMn$_x$O$_3$ ($x=0.05$) | 2 | 6 | 0.05 | 0.036 |
| NaCo$_2$O$_4$ | 3 | 12 | 0.5 | 0.032 |
| La$_{1-x}$Sr$_x$TiO$_3$ ($x=0.05$) [2] | 2 | 40 | 1.2 | 0.032 |
| Bi$_2$Te$_3$ | 1 | 45 | 200 | 1.2 |

Table 1: Comparison of the thermoelectric performances of the different oxides studied here with the best thermoelectric materials.

The manganese oxides investigated here have similar properties as the other thermoelectric oxides. By chosing the right dopant, the different factors of Z can be tuned to optimize it: Ru is promising as it introduces disorder among the Mn ions and reduces $\kappa$, it favors metallicity because of its electronic structure, and last the reduction of S linked to the improved metallicity is not too large at room temperature because of its mixed valency. Furthermore, as in the case of NaCo$_2$O$_4$, a large reduction of $\rho$ is expected in the case of single crystals which could strongly improve Z. The negative thermopower makes them interesting as n leg for a thermoelectric device. Indeed, it has been very recently reported that Ca$_{0.92}$La$_{0.08}$MnO$_3$ has already been used to design a thermoelectric power generator with promising performances [3].

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