Search for p-type oxide thermoelectrics - cobaltites

H. Fujishiro^{1*}, Y. Fujine¹, J. Hejtmanek², D. Sedmidubsky², A. Maignan³, and C. Martin³

¹ Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan

² Institute of Physics of ASCR, Cukrovarnivka 10, 16200 Praha 6, Czech Republic

³Laboratoire CRISMAT, CNRS/ISMRA/Universite de Caen, 6 boulevard du Maréchal Juin, 14050 CAEN cedex, France

*email: fujishiro@iwate-u.ac.jp, fax: +81-19-621-6373

Abstract The thermal conductivity, thermoelectric power, electrical resistivity and magnetization of the 3D perovskites $Ln_{1-X}AE_XCoO_3$ (Ln=La,Y and AE=Ca and Ba) and the low dimensional Ca₃Co₂O₆ and Ca₃Co₄O₉ cobaltites were measured in a wide temperature range up to 1000 K. As a novelty we demonstrate the prospective high power factor of the Y_{0.9}Ca_{0.1}CoO₃ at high temperatures and, simultaneously, that in the La_{1-X}AE_XCoO₃ system the maximum Z and P values are observed at the phase boundary between the FM and SG state at X~0.1 and exceed that reported for layered cobaltite ceramics.

1. Introduction

Two important points are to be solved prior the application of the material in the thermoelectric device: - a high figure of merit ZT (= $S^2/\kappa\rho$; S the thermoelectric power, κ the thermal conductivity, ρ the electrical resistivity) and the long term chemical stability. Within a large family of conducting oxides the complex cobaltites are of the fundamental importance as candidates for the high temperature p-type thermoelectric applications. This is due the unusual concurrence of a high electrical conductivity and a high positive thermoelectric power. Consequently, the layered Co-based oxides such as NaCo₂O₄ [1], Ca₃Co₄O₉ [2] and Bi_{2-x}Pb_xCo₂O_y [3] have recently attracted much attention as thermoelectric materials with a high figure of merit Z and power factor P (= S^2/ρ).

Within the family of conducting cobalt oxides, however, two sub-groups of octahedrally coordinated cobalt networks (CoO₆) can be distinguished: (i) the first one, mentioned above, represented by low dimensional 2D or 1D compounds where the dominating Co-O-Co bond is mediated via edge/face shared octahedra and (ii) with corner shared (CoO₆) octahedra represented by a large perovskite family.

We exemplify the thermoelectric properties of the representative oxides $Ca_3Co_2O_6$ and $Ca_3Co_4O_9$ but the main significance is focused on perspectives 3D perovskites which thermoelectric performance was up to now marginalized with respect to a very promising bronze-like $NaCo_2O_4$. We present the experimental data on thermal conductivity, thermoelectric power, electrical resistivity and magnetism determined in a wide temperature range from low temperatures up to 1000 K. The possible link between a high thermoelectric power and various spin (*e.g.* Co^{3+} in a low-LS, intermediate-IS and high spin-HS) eventually orbital ($e_g = d_z^2$, $d_x^2-y^2$) fluctuations is discussed as the high degeneracy of Co spin state has been pointed out as a possible origin of the large *S* values [4].

The studied $Ln_{1-X}AE_XCoO_3$ (Ln=La,Y and AE=Ca and Ba) systems crystallize a perovskite structure, which, in dependence of the size of interpolated cation adopts either *Pbnm* or *R3c* symmetry. Although the cobalt perovskites have been investigated for a long time, there is no systematic report as for the thermoelectric potential as far as we know. Let us remember that in the parent material LaCoO₃, the transition from the low spin of Co³⁺ (LS; S=0)

to intermediate-spin (IS; S=1) configuration was evidenced at T~100 K when the origin of successive transition at T~500 K, accompanied by huge increase of electrical conductivity, is not unambiguously elucidated. As most plausible scenario the spin origin (IS=>HS), orbital order (IS Jan-Teller distorted => IS non distorted) or Mott-like MI transitions were proposed. Due to the introduction of Co⁴⁺ species a ferromagnetic metallic (FM-M) ground-state appears in Ln_{1-X}AE_xCoO₃ for $X \ge 0.2$. On the other hand, the cobalt ions in YCoO₃ are known to preserve the LS ground-state up to temperatures well above 300 K, while the impact of Co⁴⁺ species, introduced via the Ca for Y substitution, on the long range magnetic order is not known.

2. Experimental

Polycrystalline samples of Ca₃Co₂O₆ and Ca₃Co₄O₉ were prepared by a standard ceramic route [5]. The post annealing in oxygen, which were used to ensure the oxygen stoichiometry in Ca₃Co₂O₆ sample, led however to the formation of the "misfit" Ca₃Co₄O₉ phase. Coherently with the detection of the $Ca_3Co_4O_9$ phase by means of X-ray the bi-phasic nature of Ca3Co2O6 post-annealed samples was confirmed by transport measurements as further demonstrated in Fig. 1. The perovskites La1-xAExCoO3 $(0 \le X \le 0.40; AE = Ca, Ba))$ and $Y_{1-X}Ca_XCoO_3$ $(0 \le X \le 0.20)$ were prepared by a solid-state or nitrate decomposition method, respectively. The samples were heat-treated in flowing oxygen at 900°C for 24 h in order to achieve the oxygen stoichiometry and the measured densities of samples were about 85~90 % of the ideal ones. The X-ray diffraction analyses at room temperature confirmed that all La-based samples were a single rhombohedral phase and Y-based samples posses the Pbnm symmetry. The electrical resistivity ρ was measured by a standard four terminal method. The thermal conductivity κ and thermoelectric power S were measured in close cycle cryostat by a steady-state 4-point heat flow method [6]. The high temperature measurement was performed using home made apparatus in air. The magnetization M was measured using a SQUID magnetometer and the Hall coefficient was measured at room temperature using the 5 T cryo-cooled superconducting magnet to estimate the carrier concentration n.

3. Results and Discussion

3.1 Low dimensional cobaltites

The electric and thermal transport data of 1D and 2D representative cobaltites are presented in the Fig. 1. The gradual evolution from the essentially insulating 1D system, which exhibit the huge positive thermopower, to quasimetallic 2D layered cobaltite is clearly evidenced. At very high temperatures the high potential for thermoelectric applications of 1D cobaltite is underlined by a high thermopower of ~ +300 μ VK⁻¹ compensated, however, by

still high resistivity of ~ 100 m Ω cm. Let us note also the presence of low temperature enhancement of thermal conductivity, observed for pure Ca₃Co₂O₆, which is typical for crystalline solids. This phononic peak is evidently suppressed in layered cobaltite exhibiting "glass-like" behavior of thermal conductivity.

Fig. 1. The temperature dependence of the electrical



resistivity $\rho(T)$ (upper panel), thermoelectric power S(T)(middle panel) and (c) thermal conductivity $\kappa(T)$ (lower panel) of $Ca_3Co_2O_6$ (), intergrowth of $Ca_3Co_2O_6$ and $Ca_4Co_3O_9(O)$ and $Ca_4Co_3O_9(\Delta)$.

As concerns the high and weakly temperature dependent thermoelectric power of these cobaltites at high temperatures we propose is to link its absolute value with configurational entropy of "hopping" hole-like charge carriers where the decisive contribution to the thermopower originates from an interplay of the number of charge carriers (x) and the difference in the degeneracy $\beta = \underline{g_3}$ between Co³⁺ and Co⁴⁺ species, respectively. The g_4

generalised Heikes formula S =]

$$-\frac{\kappa_B}{e} \ln \left[\beta, \frac{x}{1-x}\right]$$

supposes that dominating contribution to the thermopower is the configurational entropy of quasi-degenerate charge carriers. The detailed analysis of this formula is, however, out of the scope of this paper. Nonetheless it is evident that the high thermopower can be achieved either as a result of a low hole concentration (small x) or a high difference between the spin and orbital degeneracy of the Co sites without (Co^{3+}) or with (Co^{4+}) a hole. Based on photoemission studies of the misfit cobaltites [7] complemented by magnetic susceptibility measurements [8], both Co^{3+} and Co⁴⁺ are found to be in the low spin states. This allows to derive additional contribution to the thermopower with $\beta = 1/6$ providing huge thermopower enhancement of ~+154

 μVK^{-1} over the basic value defined by charge carrier concentration.

3.2 Y_{1-X}Ca_XCoO₃ (0≤X≤0.20) system

Magnetic, structural and transport properties were investigated over a broad temperature region up to 1000 K. The temperature dependence of magnetic susceptibility is in Fig. 2 compared with lines marking the characteristic spin states. The magnetic susceptibility data shows that the Ca doping does not induce the significant change of magnetic behaviour and both presented samples, x=0.0 and x=0.1, preserve the low-spin ground-state up to \sim 400 K. Contrary to published data on LaCoO₃, the high temperature metal insulator transition is evidently not associated with a IS=>HS spin state transition but is accompanied only by the gradual increase to the intermediate spin state with S=1. Nonetheless, in distinction to the magnetic data, where the Ca doping does not induce a significant modifications, the important impact of the Ca to Y substitution on the resistivity and thermoelectric power can be mentioned - see upper and middle panel of Fig. 2. Thus, as a consequence of significantly reduced electrical resistivity upon the Ca doping the high temperature power factor, depicted in Fig. 5, reaches the promising values. In that case, contrary to the low dimensional cobaltites where the important role of spin and orbital degeneracy was emphasized, the high value of thermoelectric power is conditioned by a low concentration of charge carries.



Fig. 2. The temperature dependence of the electrical resistivity $\rho(T)$ (upper panel), thermoelectric power S(T)(middle panel) and (c) magnetic susceptibility $\chi(T)$ (lower panel) of Y₁₋xCa_xCoO₃.

3.3 La_{1-X}Ca_XCoO₃ and La_{1-X}Ba_XCoO₃ system

In Fig. 3 and Fig. 4 we show the temperature dependence of the electrical resistivity, thermoelectric power and magnetic moment measured at 0.5 T of and $La_{1-X}Ba_{X}CoO_{3}$ (0.1 \leq X \leq 0.40), $La_{1-X}Ca_XCoO_3$ respectively. The incorporation of formally Co⁴⁺ species via AE^{2+} substitution leads to the appearance of FM component below 200 K and, simultaneously, to the metallic-like behaviour of thermoelectric power. In the case of La-Ca system, however, the positive and weakly temperature dependent S(T) value reduces suddenly for X>0.20. Simultaneously the resistivity is depressed down to ~1 m Ω cm but at low temperature the localization occurs

up to X=0.40. The ferromagnetism is more pronounced in case of La-Ba system with the tolerance factor Γ of the significantly larger than that of the LaCa-system. Coherently with a high metallic electrical conductivity of ferromagnetic samples the S(T) reaches very small values typical for metallic thermopower. Nonetheless the direct association of the decreased thermopower due to the decrease of the spin degeneracy of Co ions is also not excluded see. e.g. sample X=0.2 which exhibit activated electrical resistivity below T_C but thermopower is close to zero.



Figure 3: The temperature dependence of the electrical resistivity (a), thermoelectric power (b) and magnetic moment (at 0.5 T) (c) of the La_{1-X}Ca_XCoO₃ ($0.1 \le X \le 0.40$).

We demonstrate in the Fig. 5 the temperature dependence of the power factor P(T) for $Y_{1-X}Ca_XCoO_3$, $La_1Ca_XCoO_3$ and $La_1Ba_XCoO_3$. The P(T) value of $Y_{1-X}Ca_XCoO_3$ is low at 300 K, but is enhanced at the phase boundary of metal-insulator (M-I) transition (T=700 K) in case of X=0.1 sample which makes this system promising with respect to a high temperature applications. The maximum P(T) value of $La_1Ca_XCoO_3$ is obtained for X=0.15, but that of $La_1Ba_XCoO_3$ for X=0.10. This differences can be linked with different tolerance factor values of both systems.



Figure 4: The temperature dependence of the electrical resistivity (a), thermoelectric power (b) and magnetic moment (at 0.5 T) (c) of the La_{1-X}Ba_XCoO₃ ($0.1 \le X \le 0.40$).



Figure 5: The temperature dependence of the power factor P(T) of (a) Y_{1-X}Ca_XCoO₃, (b) La₁Ca_XCoO₃ and (c) La₁Ba_XCoO₃.

In the Fig. 6 we summaries the X dependence of Z for $La_{1-X}AE_XCoO_3$ (AE=Ca,Sr,Ba) at room temperature. A clear sharp maximum can be seen at around X=0.10 for all systems. However, Z for the $La_{1-X}Ca_XCoO_3$ system exhibits a broadened X dependence and the corresponding calcium concentration $X(Z_{max})$ is larger. It is to be noticed that the ionic radius of the Ca^{2+} ion is smaller than those of Sr^{2+} and

Ba²⁺ enhancing then the lattice distortion and hindering the degeneracy of charge carriers.

The maximum Z and P values of the $La_{1-X}AE_XCoO_3$ system are higher than those of layered cobaltites, which have recently been investigated vigorously. In the Fig. 7 we show the comparison of P(T) based on our data and the reported values of typical layered cobaltites. The P(T)values of $La_{1-X}Ba_XCoO_3$ (X=0.10) and $La_{1-X}Ca_XCoO_3$ (X=0.15) are confronted with ceramic Ca₃Co₄O₉ [2], single-crystalline Bi_{2.3-X}Pb_XSr_{2.6}Co₂O_y (X=0.44) [3], ceramic NaCo₂O₄ [9], and ceramic NaCo_{2-x}Cu_xO₄ [10]. Although our P values are about one order of magnitude smaller than that for the NaCo₂O₄ single crystal (~5 mW/K^2m ; [1]), the present P values are larger than those of the other layered cobaltites prepared by ceramic technology. Let us underline that the largest P(T) values are observed for $X \sim 0.1$, where the magnetic properties changes from the spin-glass state to the FM state.



Figure 6: The *X* dependence of *Z* for $La_{1-X}Ca_XCoO_3$, $La_{1-X}Sr_XCoO_3$ and $La_{1-X}Ba_XCoO_3$ systems at 300 K.



Figure 7: P(T) of the studied perovskites (La_{0.90}Ba_{0.10}CoO₃ and La_{0.85}Ca_{0.15}CoO₃) confronted with the reported values of the typical layered cobaltites (Ca₃Co₄O₉ [2], Bi_{2.3-X}Pb_XSr_{2.6}Co₂O_y (*X*=0.44) [3], NaCo₂O₄ [9] and NaCo_{2-X}Cu_XO₄ [10]).

4. Conclusions

The thermoelectric properties of three cobalt perovskite systems ($Y_{1-x}Ca_xCoO_3$ ($0 \le X \le 0.20$) and $La_{1-x}AE_xCoO_3$ ($0 \le X \le 0.40$, AE=Ca, Ba)) as well as the low dimensional cobaltites ($Ca_3Co_2O_6$ and $Ca_4Co_3O_9$) have been measured and analyzed. Important experimental results and conclusions obtained in this study are summarized as follows.

- (1) In the 1D and layered cobaltites the important part of thermoelectric power up to 1000 K is associated with configurational entropy of low spin Co^{3+} and Co^{4+} configurations
- (2) The Y_{0.9}Ca_{0.1}CoO₃ exhibit promising termoelectric properties up to 700 K
- (3) For the La_{1-X}AE_xCoO₃ system (AE=Ba, Sr, Ca), the figure of merit Z and power factor P increase with increasing AE concentration X and peaks at X=0.10 and decreases for higher X. The maximum Z is observed at the phase boundary between the FM and SG state. At 300 K, the best Z and P values are larger than those of layered cobaltites such as Ca₃Co₄O₉, NaCo_{2-X}Cu_xO₄.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of the Education, Culture, Sports, Science and Technology, Japan (No. 14550661) and by program KONTAKT ME 572 of the Ministry of Education, Youth and Sports of the Czech Republic.

References

- Terasaki, I. et al, Phys. Rev. B, Vol. 56 (1997), pp. R12685-R12687.
- 2. Masset, A.C. et al, Phys. Rev. B, Vol. 62 (2000), pp. 166-175.
- Ito, T. *et al, Jpn. J. Appl. Phys.*, Vol. 39, No. 12A (2000), pp. 6658-6660.
- 4. Koshibae, W. et al., Phys. Rev. B, Vol. 62 (2000), pp. 6869-6872.
- 5. D. Pelloquin et al, Chem. Mater. 2002, 14, 3100-3105
- 6. Fujishiro, H. *et al.*, *Cryogenic Engineering*, Vol. 28 (1993) pp. 533-539 (in Japanese).
- 7. T. Mizokawa et al, *Phys. Rev. B*, Vol 64, (2001), pp 115104.
- 8. Tsukada et al. J. Phys. Soc. Jap. 70, (2001), 834.
- 9. Takahata, K. et al, Phys. Rev. B, Vol. 61 (2000), pp. 12551-12555.
- 10. Terasaki, I. et al, Jpn. J. Appl. Phys., Vol. 40 (2001), pp. L65-L67.