Thermoelectric Power In Misfit Cobaltites Ceramics: Optimization By Chemical Substitutions

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The ceramics of misfit cobaltites form a large family of layer oxides which exhibit large values of Seebeck coefficient ($S_{300K} \geq 90 \mu V.K^{-1}$). They can be divided in two categories depending on the number of the rocksalt-type (RS) layers, n = 3 or n = 4, separating the [CoO$_2$] conducting layers. From the comparison of their structural features, it is found that the S values are governed by the incommensurability ratio and/or the charge of the RS block. This is clearly evidenced by making chemical substitutions at the level of the RS block: isovalent but with cations of different ionic radius ($r_{Ba}^{2+} > r_{Sr}^{2+} > r_{Ca}^{2+}$) modifying the incommensurability ratio or aliovalent substitutions for cobalt (Pb^{4+}, Ti^{4+}) which keep unchanged the structural incommensurability but make the RS charge changing.

Keywords: thermoelectric power, cobaltites, chemical substituons.

Potencia termoeléctrica de cerámicas basadas en cobaltitas: optimización mediante sustitución química.

Las cerámicas basadas en cobaltitas forman una extensa familia de óxidos que presentan valores elevados del coeficiente seebeck ($S_{300k} \geq 90 \mu V.K^{-1}$). Se pueden dividir en dos grupos dependiendo del número de capas con estructura de cloruro sódico (rocksalt - RS), n=3 ó n=4, que separan las capas conductoras de [CoO$_2$] . Comparando sus caractetísticas estructurales, se ha encontrado que los valores de S están gobernados por la relación de inconmensurabilidad y la carga del bloque con estructura RS. Esto se evidencia claramente realizando sustituciones químicas en los bloques RS: Isobalentes con cationes de diferente radio ($r_{Ba}^{2+} > r_{Sr}^{2+} > r_{Ca}^{2+}$) que modifican la relación de inconmensurabilidad o sustituciones aliovalentes de cobalto (Pb^{4+}, Ti^{4+}) que provocan cambios en la carga del bloque RS pero no en la inconmensurabilidad.

Palabras clave: potencia termoelectrica, sustituciones químicas.

1. INTRODUCTION

The 'misfit' cobaltite $Ca_3Co_4O_9$ [1] shows a very good chemical stability up to at least 1000K, and, thus, is a promising thermoelectric material to be used as a p-leg in thermogenerator to convert waste-heat into electricity [2]. This phase belongs to a large family of layer oxides which structure consists in alternating CoO_2 layers and rock-salt (RS) type layers [3]. The structure of the former are of the CdI_2-type with edge-shared CoO_6 octahedra and the number of RS-type layers can be either n = 3 or n = 4. Their CoO_2 planes are isostructural to those found in the T_c = 5K superconductor, $Na_{0.35}CoO_2$, $1.3H_2O$ [4].

The complexity of the misfit structures comes from the aperiodic character of the two monoclinic sublattices RS-and CdI_2-types which b cell parameters are incommensurate [5]. In analogy with the structures of superconducting cuprates also made of n x RS type layers, separating blocks of perovskite layers and represented as $[A'O]_n^{RS}[ACuO_3]_{m'}$ the chemical formulas of the misfit cobaltites can be written $[AO]_n^{RS}[CoO_2]_{b1/b2}$ where b_1 and b_2 are the b cell parameters of the two RS-and CdI_2-type monoclinic sublattices, respectively.

The extraordinary richness of this series of compounds is due to the possibility to introduce numerous cations in the RS-type separating layers. But, as a result, the cobalt exhibits also a tendency to be incorporated not only in the CoO_2 conducting layers but also in the RS-type layers, as illustrated by the chemical formula $[Ca_2CoO_3]^{RS}[CoO_2]_{1.62}$ of "$Ca_3Co_4O_9$". This makes very difficult the extraction of the cobalt oxidation states at the level of the CoO_2 layers, since the two different cobalt crystallographic sites may be occupied by different types of cobalt cations. Nevertheless, several chemical substitutions can be made in these complex oxides which are found to change their Seebeck coefficients. For instance, isovalent substitutions at the level of the RS-type block can be used to make varying the cell parameters of this sublattice without changing its total charge.

In the following, we report on the relationship between structural features and Seebeck coefficient S values for several ceramic samples containing 3 or 4 RS-type layers and whose structures and cationic compositions have been determined by combining X-ray and electron diffraction to Energy Dispersive X-ray Spectroscopy (EDS) analysis. An attempt to relate S to the cobalt oxidation state in the CoO_2 layer is also given.

2. EXPERIMENTAL SECTION

The preparation condition of the samples under study have been previously reported in ref. [1, 5-7]. These polycrystalline

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materials are prepared by conventional solid state reaction. The n = 4 members are prepared by mixing the Bi_2O_3, PbO, $AeCO_3$ (Ae = Ca^{2+}, Sr^{2+}, Ba^{2+}) and $CoO_{4/3}$ precursors in stoichiometric ratio according to the cation content in the chemical formula. After decarbonation and then addition of the Bi_2O_3 (and/or PbO) oxide, bars of 2 x 2 x 10mm typical dimensions are obtained by pressing under 1 ton/cm². The so-obtained bars are then sintered in air at 850°C - 900°C for 12 hours. The n = 3 members are prepared by using closed quartz ampoules, i.e. using CaO, SrO_2 or BaO_2 instead of carbonates. About 1g of bars with the desired cation content is put in a finger-like alumina crucible. The latter, set in a quartz tube, is sealed under primary vacuum. The obtained closed tubes are heated at ~ 900°C for 12h. The structure of the as-prepared black bars is studied by combining X-ray and electron diffractions (ED) and also EDS analyses coupled to electron diffraction, are used to determine the cation contents. Then from structural refinements of X-ray diffraction data combined to ED and EDS results, the $[AO]^{RS}_n$ $[CoO_2]_{b1/b2}$ formula is obtained. The Seebeck values are measured on the aforementioned ceramic bars in between 5K and 310K by a steady-state technique [8].

3. RESULTS

3.1 Bi-based n= 4 misfit compounds: steric effect on the S value.

The different phases belonging to this family contain RS-type layers such as [AeO]-[Bi(Co)]-[Bi(Co)]-[AeO] where Ae is for the alkaline earth cation, Ba^{2+} [7] or Sr^{2+} [5] or Ca^{2+} [6]. Interestingly, their ionic radii are such as $r_{Ba}^{2+} > r_{Sr}^{2+} > r_{Ca}^{2+}$ so that the b_1 cell parameter of the RS lattice decreases as one goes from Ba^{2+} to Ca^{2+}. Since the b_2 parameter is left almost unchanged by the change of Ae cation , the b_1/b_2 ratio increases as the Ae ionic radius increases, from an incommensurate value b_1/b_2 = 1.67 for Bi/Ca/Co/O to a commensurate value b_1/b_2 = 2.00 for Bi/Ba/Co/O. As one plots the S values as a function of the b_1/b_2 ratio (Fig.1), it becomes obvious that S decreases as the b_1/b_2 ratio increases. These values are taken from the S(T) curves of Fig. 2. By making the rough assumption that the total electrical charge of the RS-type slab does not change as one goes from Ba^{2+} to Ca^{2+} through Sr^{2+}, the decrease of the b_1/b_2 corresponding ratio induces a decrease of the oxidation state for the cobalt species in the $[CoO_2]$ type layers. For electroneutranility reason, the
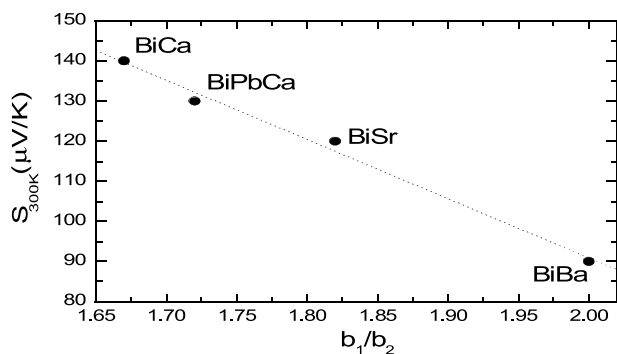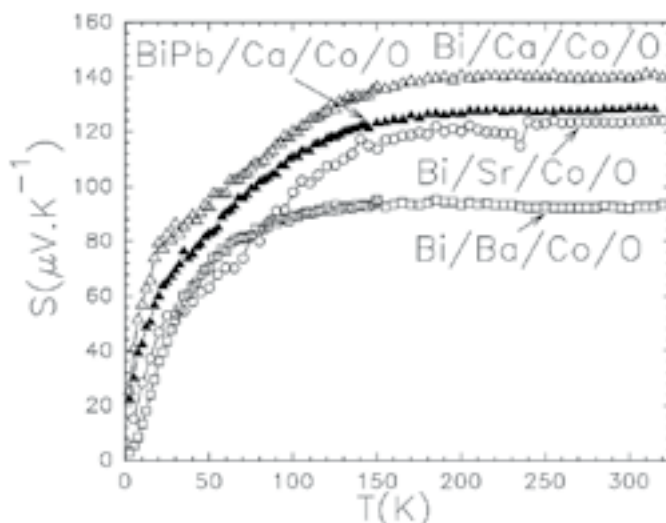

Fig. 2- T dependence of the thermoelectric power TEP; (Seebeck coefficient, $S = \dfrac{\Delta V}{\Delta T}$)

charge of the RS block positive and constant Ch_{RS} must be equal to the negative charge of the CdI_2 block ($Ch_{CdI2} = V_{Co} - 4$, where V_{Co} is the oxidation state of cobalt minus the charge of the $Z0^1$). Taking into account the $[RS][CdI_2]b\lambda/b_2$ formula this yields $V_{Co} = 4 - \dfrac{Ch_{RS}}{b_1/b_2}$.

Following then the Koshibae's expression, relating S to the fraction of Co^{4+} over the total amount of cobalt [9], and plotted in Fig. 3, it becomes clear that the decrease of the number of holes in the CoO_2 layer induces a S increase (table I).
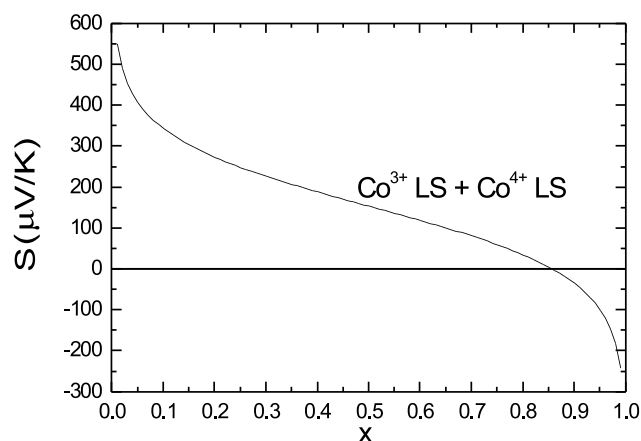

Fig. 3- Seebeck coefficient (S) plotted as a function of the fraction of Co^{4+} (x) from the Koshibae's expression $S = -\dfrac{k_B}{e} \ln\left(\dfrac{1}{6} \times \dfrac{x}{1-x}\right)$. LS is for low spin.

Fig. 1- Seebeck coefficient values at 300K as a function of the b_1/b_2 ratio for the $[(Bi/Co/AeO)_4]^{RS}[CoO_2]_{b1/b2}$ n = 4 misfit compounds; Ae = Ba^{2+}, Sr^{2+}, Ca^{2+}.

TABLA I. n=4 MISFIT COBALTITES: CHEMICAL FORMULA, B_1/B_2 INCOMMENSURABILITY RATIO, VALUE OF THE SEEBECK COEFFICIENT S_{300K} AND COBALT OXIDATION STATE V_{CO} FOR THE COO_2 LAYER CALCULATED FROM KOSHIBAE'S RELATION.

	b_1/b_2	S_{300K} ($\mu V.K^{-1}$)	v_{Co}
$[Bi_{1.7}Co_{0.3}Ca_2O_4]^{RS}[CoO_2]_{1.67}$	1.67	140	3.54
$[Bi_{1.3}Pb_{0.6}Co_{0.2}Ca_{1.9}O_4]^{RS}[CoO_2]_{1.72}$	1.72	128	3.58
$[Bi_{1.62}Co_{0.38}Sr_2O_4]^{RS}[CoO_2]_{1.82}$	1.82	110	3.63
$[Bi_2Co_{0.2}Ba_{1.8}O_4]^{RS}[CoO_2]_2$	2.00	92	3.68

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It must be pointed out that in this series of misfit compounds, the Pb substitution for Bi in the Bi/Ca/Co/O phase induces a b_1/b_2 increase from 1.67 to 1.72 which also obeys the $S(b_1/b_2)$ linear relation given in Fig. 1.

3.2 n = 3 misfit phases: aliovalent and isovalent substitutions.

Starting from the first reported member, $[Ca_2CoO_3]^{RS}[CoO_2]_{1.62}$, also called "$Ca_3Co_4O_9$", we showed that the S value can be increased from S = 125μV.K^{-1} to S = 165μV.K^{-1} by aliovalent substitutions which do not modify the b_1/b_2 ratio [10]. The S(T) curves of these n = 3 misfit cobaltite is shown in Fig. 4. Referring to our previous discussion for the n = 4 members, an increase of S, i.e. a decrease of the cobalt oxidation state in the $[CoO_2]$ conducting slab, in two compounds characterized by the same b_1/b_2 ratio, implies that the charge of the RS-type block increases. In the $[Ca_2Co_{1-x}Pb_xO_3]^{RS}[CoO_2]_{1.62}$ series [10], this means that lead is tetravalent. This assumption is confirmed by the S increase observed for substitutions by tetravalent cations such as Ti^{4+} (or Sn^{4+}) (see Table II).
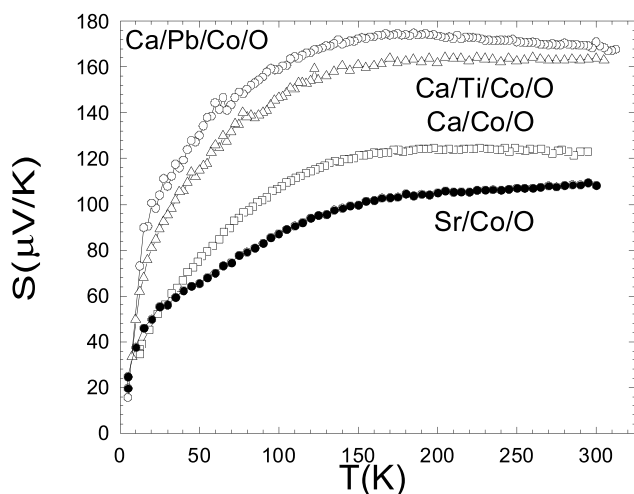

Fig. 4- S(T) curves of the n = 3 misfit cobaltites

TABLA II. n = 3 MISFIT COBALTITES CHEMICAL FORMULA, B_1/B_2 INCOMMENSURABILITY RATIO, VALUES OF THE SEEBECK COEFFICIENT S_{300K} AND COBALT OXIDATION STATE V_{Co} FOR THE COO$_2$ LAYER CALCULATED FROM THE KOSHIBAE'S RELATION.

	b_1/b_2	S_{300K} (μV.K^{-1})	v_{Co}
$[Ca_2CoO_3]^{RS}[CoO_2]_{1.62}$	1.62	125	3.59
$[Ca_2Co_{0.6}Pb_{0.4}O_3]^{RS}[CoO_2]_{1.62}$	1.62	165	3.47
$[Ca_2Co_{0.6}Ti_{0.4}O_3]^{RS}[CoO_2]_{1.62}$	1.62	160	3.48
$[Sr_2CoO_3]^{RS}[CoO_2]_{1.80}$	1.80	110	3.63

Now, by fixing arbitrarily the cobalt valency at $v_{Co}^{RS} = 3$ for the cobalt in the RS-type layers, one can simply deduce the cobalt valency in the $[CoO_2]$ layer. This leads to v_{Co} = 3.38 and v_{Co} = 3.14 for $[Ca_2CoO_3]^{RS}[CoO_2]_{1.62}$ (x = 0.00 sample) and $[Ca_2Co_{0.6}Pb_{0.4}O_3]^{RS}[CoO_2]_{1.62}$ (x = 0.4 sample). Independently, knowing the S values one can also extract the v_{Co} values from

the modified Heikes formula plotted in Fig. 3. One obtains $v_{Co} = 3.59$ and $v_{Co} = 3.47$ for the x = 0 and x = 0.4 samples, respectively. Although the values extracted from the chemical formula and the Seebeck coefficients differ, in both series a similar trend for v_{Co} is found.

4. DISCUSSION AND CONCLUDING REMARKS

Comparison of n = 3 and n = 4 members shows that the cobalt valency in the $[CoO_2]$ layer of misfit cobaltites can be varied by changing the b_1/b_2 ratio and/or the oxidation states of substituting cations at the level of the RS-type block. The discovery of the $[Sr_2CoO_3][CoO_2]_{1.8}$ compound [11], isostructural to $[Ca_2CoO_3]^{RS}[CoO_2]_{1.62}$, confirms these conclusions. Again, the isovalent Sr^{2+} for Ca^{2+} substitution makes increase the b_1/b_2 ratio, which is expected to decrease the Seebeck coefficient value according to the aforementioned relation $V_{Co} = 4 - \dfrac{Ch_{RS}}{b_1/b_2}$. As shown in Table II, this is exactly what is measured, S decreasing from 125μV.K^{-1} down to 110μV.K^{-1} from 'Ca' to 'Sr' misfit n = 3 members, respectively.

At first glance, despite the complex structures of the misfit cobaltites, the Seebeck coefficient values of both n = 3 and n = 4 members of this family depends on the cobalt valency (v_{Co}) of the cations located in the CoO_2 layer. Chemical substitutions in the RS-type block allow to modify the total charge of this block, which is compensated by adjusting v_{Co} in the $[CoO_2]$ layer and/or change the cell parameters of the RS-type sublattice, which creates a shift on the b_1/b_2 value inducing a different v_{Co} value. However, these conclusions have been established on the basis of structural electron microscopy studies which are necessary to obtain the cation compositions from EDS analysis coupled to electron diffraction and on the basis of refinements of the X-ray diffraction data to extract the b_1/b_2 incommensurability ratio. These structural studies show also that a large amount of cations can be substituted in the RS-type layers of these compounds, allowing to reach the largest S values.

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