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SOLAR-TEP

SOLARE THERMOKRAFT

Final Report

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Zusammenfassung

Die direkte und effiziente Umwandlung von thermischer (Solar)-Energie in elektrische Energie erfordert die Entwicklung thermoelektrisch aktiver p- und n- Halbleitermaterialien, die in Luft auch bei hohen Temperaturen stabil sind. Hochtemperaturwandlungen sind attraktiv, da die resultierende Thermospannung zwischen zwei Enden eines Thermoelektrikums proportional zur angelegten Temperaturdifferenz ist. Um einen möglichst hohen Wirkungsgrad für die Energiewandlung zu erzielen, sind Materialien erforderlich, die neben grosser Thermokraft und grosser elektrischer Leitfähigkeit eine niedrige Wärmeleitfähigkeit aufweisen. Es konnte im Verlauf des Projektes gezeigt werden, dass keramische Materialien mit Perowskitstruktur diese Anforderungen erfüllen. In dieser Substanzklasse wurden an der Empa eine Vielzahl p-leitender und n-leitender Verbindungen entwickelt, welche je nach Zusammensetzung grosse Thermokraft mit sowohl positivem Vorzeichen, als auch mit negativem Vorzeichen aufweisen. Ihre sehr gute thermische Stabilität in Luft konnte in thermoelektrischen Testmessungen und thermogravimetrischen Experimenten verifiziert werden und zeigt, dass diese Substanzen für Anwendungen bei Temperaturen um 1000 °C hervorragend geeignet sind. Die thermoelektrischen Eigenschaften dieser Keramiken konnte u.a. durch strukturelle und morphologische Änderungen gezielt beeinflusst werden.

Strukturelle Untersuchungen erfolgten sowohl an der Empa als auch an Grossforschungsanlagen mittels Röntgen- und Neutronendiffraktion, Transmissionselektronenmikroskopie, Synchrotronbasierte Absorptionsspektroskopie, und Ramanspektroskopie.

Abstract

The direct and efficient conversion of concentrated solar radiation into electricity with high power output requires the development of thermoelectrically active *p*- and *n*-type semiconductors with similar materials properties which are stable in air at very high temperature. The only suitable materials to fulfil this task are high performance ceramics. We successfully developed and investigated novel perovskite-type transition metal- oxides as potential candidates for thermoelectric devices operating at high temperatures as they can possess large positive as well as large negative thermopower depending on their composition. The three parameters defining the thermoelectric figure of merit ZT are in most cases interdependent: The thermopower increases with increasing resistivity. The heat conductivity increases with electric conductivity. Therefore an optimum charge carrier concentration and mobility has to be defined, which depends on the substitution level, the spin states of the transition metals, the ligand field, i.e. the crystallographic structure, the valence states of the cations and ionic deficiencies. The tuning of the thermoelectric properties of the perovskite-type candidates is based on controlled anionic and cationic substitutions. The resulting products are characterised concerning structure and composition with diverse methods available at Empa and at large scale facilities including Xray and Neutron Diffraction, transmission electron microscopy, thermal analysis, synchrotron radiation based techniques (EXAFS, XANES, Diffraction) as well as Raman spectroscopy and tested concerning their thermoelectric activity in the novel thermoelectricity lab at Empa.

1. Introduction

Thermoelectric (TE) conversion technologies were identified in the USA and in Japan as being indispensable for waste heat recovery and deep space missions. Large governmental programs with a budget in the range of billions of dollars were launched in these countries to support materials research in the field.

In general, the performance of TE materials is evaluated using the thermoelectric figure of merit ZT which should be around unity for very good thermoelectrics. Most of the developed materials are not applicable at T>600°C where the power output becomes interesting.

The recent discovery of large thermopower in perovskite-type oxides showed the potential of oxides for TE applications, because ceramic materials are more stable, less toxic, and more cost-effective compared to conventional thermoelectric materials.

Misfit cobaltites with low phonon thermal conductivity and large electronic mobility were identified as currently one of the most promising thermoelectric materials. The misfit-layered oxides like $Ca_3Co_4O_9$ is a “phonon glass” and an “electron crystal”.

The open challenges for the realisation of high temperature TE converters include the development of thermoelectric oxides with a high figure of merit based on cheap and environmentally friendly elements.

2. Goal of Work

The goal of the project was to develop advanced materials for a direct conversion of solar heat into electrical energy by thermoelectric conversion.

3. Methods

The method to find and develop better thermoelectric materials was to first theoretically describe the advantages and disadvantages as well as the limitations of the known thermoelectrics. We found that oxide type materials are commonly identified as the most promising future thermoelectrics. All leading international thermoelectric activities include this class of materials. On international meeting the oxide community is increasing since two years, while activities on other materials development seam to stagnate. Besides oxides we chose alternatively some intermetallics and chalcogenides, but found out that they are not competitive.

The strategy of the thermoelectric materials design (see Figure 1) includes the definition of the requirements on the material and thus the choice of the material (step 1). The material has to be produced with defined composition, structure and morphology. This requires the development or tailoring of adapted synthesis procedures. Here we found that “chimie douce” (synthesis under “soft”, low temperature conditions) approaches are very suitable, because they allow the production of high surface area nanostructured compounds with a variety of compositions as well as metastable highly reactive phases which can not be obtained by classical solid state chemistry synthesis routes (step 2). Subsequently the produced materials have to be characterised thoroughly with respect to their composition-structure-property-relation (step 3) and in the end to fulfil the requirements and will therefore be tested directly in the application in an appropriate testing device. The results of these tests will have an influence on the choice of the material and will give information on the applicability of the novel functional material.

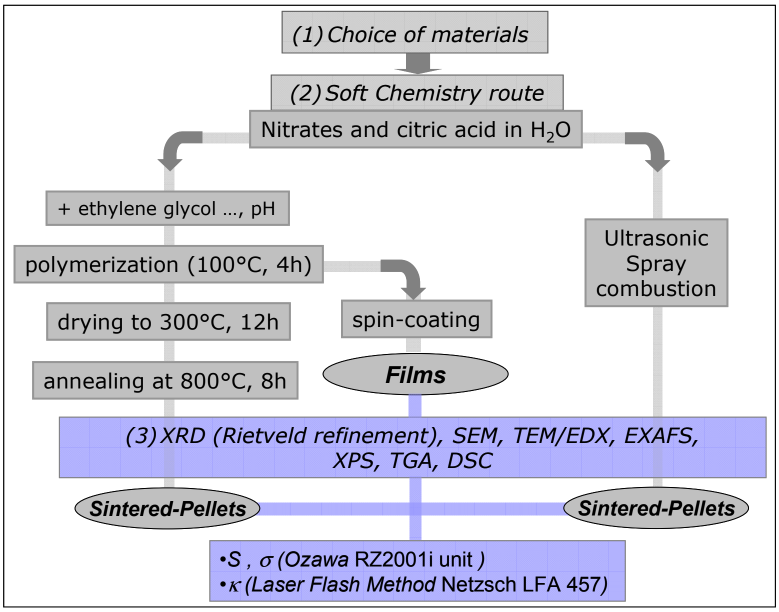

Figure 1. Flowchart for the methods of synthesis and characterization of thermoelectric materials.

(1) Choice of materials

- Half-heusler.

  18-electron half-heusler compounds e.g. NiZrSn, have attracted increasing attention as new thermoelectric materials because of their semiconductor like band structure and their high thermoelectric power.
- Nano classic thermoelectrics: n-BiTe in form of small particles
- Selenides and chalcogenides
- Metallic perovskite-type oxides: Ruthenates, layered cobaltite, manganates.
- Semi-conducting perovskite-type oxides: Cobaltates, ferrates.

(2) Soft-chemistry route

Soft-chemistry synthesis offer molecular mixing of the reactants and provide a reactive environment during the course of subsequent heating and decomposition. Thus, lower reaction temperature (873 K) and two times shorter reaction cycles compared to ceramic methods are required. Further advantages are the better control of the stoichiometry and purity, the possibility of producing new compositions and films by spin-coating, and an enhanced ability to control particle size.

(3) Characterization:

At the “Solid State Chemistry and Catalysis” group at Empa we set-up a unique equipment for the characterization of high temperature thermoelectric properties. We are able to characterize thermoelectric properties such as Sebeeck coefficient, heat and electronic transport up to temperatures of 1300 K.

The Seebeck coefficient, thermal conductivity, and electrical resistivity of the materials—key parameters to determine the thermoelectric performance of a material—are investigated and correlated to their morphology, composition, crystallinity, and microstructure.

To understand and describe new materials for thermoelectric applications, the morphology, structure, microstructure, grain size and composition of these materials is investigated. The identification of the compounds is made by x-ray powder diffraction (PANanalytical X’pert diffractometer with Cu-Kα radiation). The composition is checked by energy dispersive spectroscopy (EDS) in scanning electron microscopy (SEM equipment). The crystallinity is determined by XRD and electron diffraction (ED). Further crystallographic, grain size studies and microstructural characterization by transmission electron microscopy (TEM) is performed with a Philips CM30 (300 kV and point resolution of 2 Å).

For TE materials deposited on to a substrate by PLD, it is also necessary to perform single crystal XRD to characterize the film (crystallinity and orientation). The thin film is studied in the planar view and cross section geometry by TEM. This type of studies gives us information about the interface, defects, structure and microstructure of the thin film.

X-ray- neutron-and synchrotron diffraction techniques are essential tools to discover, identify and characterize new materials for thermoelectric applications.Neutron diffraction (ND), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments are carried out at the large–scale facilities, SINQ, SLS and HASYLAB/DESY.

Neutron diffraction and X-ray diffraction are essential tools to determine the crystal structure and space group of the material. After data evaluation by the Rietveld method, vital information, e.g. lattice parameters, atomic positions, vacancies, are obtained. EXAFS measurements become very important for structure resolution when we deal with small particle size materials. XANES is very useful tool to identify the oxidation state of the metal.

4. Results

During the period of the project several new thermoelectric materials were produced and tested at the Laboratory for Solid State Chemistry and Catalysis and the results were published in peer reviewed communications and papers.

The unique characterisation and test facilities at Empa were mounted and installed in the first period of the project, as e.g. the high temperature Seebeck measurement set-up (see figure 2).

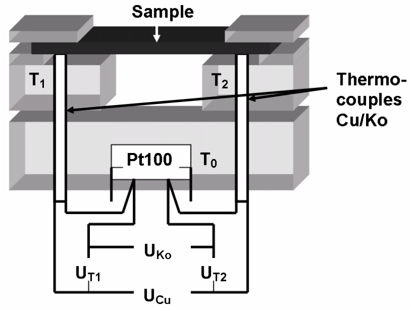

Figure 2: High temperature Seebeck and electrical conductivity measurement system at Empa

With these facilities the synthesised materials are characterised concerning their thermoelectric activity. In figure 3 some of the studied materials are compared at low and high temperature.

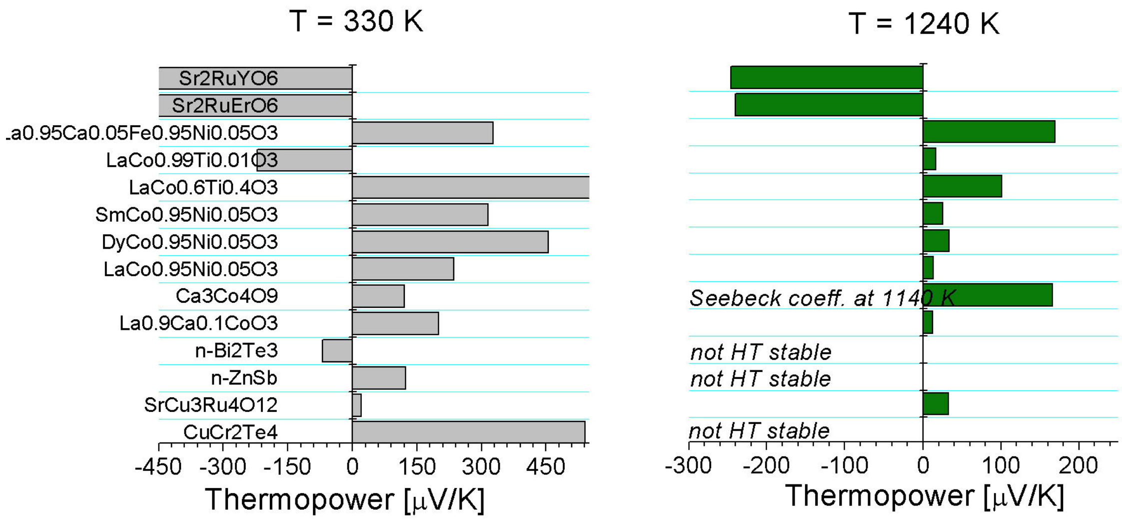

Figure 3: Measured thermopower of materials which were synthesised and characterised at Empa in the framework of the BfE solarTEP project

These studies were leading to a large database of Empa thermoelectric materials which can be applied for different thermoelectric converters. In table 1 the best thermoelectric materials developed at Empa in the time period of the BfE project are listed.

Compound	**electr. resist (mΩ*cm)**			**Seebeck coeff. (μV/K)**			**Power Factor (W/K²*m)**		
	330 K	**600 K**	**1240 K**	**330 K**	**600 K**	**1240 K**	**330 K**	**600 K**	**1240 K**
$CoTi_{0.95}Fe_{0.05}Sb$	8.85	11.7		-12	-20.8		$1.62*10^{-6}$	$3.73*10^{-6}$	
$CoTi_{0.95}Cr_{0.05}Sb$	$18.4*10^{-3}$	10.9		-62.9	-132		$2.15*10^{-5}$	$1.61*10^{-4}$	
$CoTi_{0.95}V_{0.05}Sb$	25.7	14.2		-180	-226		$1.26*10^{-4}$	$3.60*10^{-4}$	
$CuCr_2Te_4$	$33.1*10^{3}$	$4.43*10^{3}$		+541	-185		$9.28*10^{-7}$	$7.73*10^{-7}$	
$SrCu_3Ru_4O_{12}$	0.84	1.1	2.06	+20	+25	+32.5	5*10-5	5.2*10-5	$5.11*10^{-5}$
$CaCu_3Ru_{1.5}Ti_{2.5}O_{12}$	103.2	88.3	70.7	+2	+10	+17.1	$4*10^{-9}$	10^{-7}	$4.1*10^{-7}$
Sr_2RuErO_6	non	$1.5*10^{6}$	7.3	non	-312	-236	non	$6.8*10^{-9}$	$7.6*10^{-7}$
Sr_2RuYO_6	non	$2*10^{6}$	8.07	non	-409	-246	non	$8.2*10^{-9}$	$7.51*10^{-7}$
$Ca_3Co_4O_9$	9.7	9.7	10.3@ 1140 K	+120	+132	+166 @ 1140 K	$1.48*10^{-4}$	$1.8*10^{-4}$	$2.68*10^{-4}$@ 1140 K
2% Ba-$Ca_3Co_4O_9$	13.7	13.4	13.8@ 1140 K	+119	+131	+164 @ 1140 K	$1.04*10^{-4}$	$1.29*10^{-4}$	$1.96*10^{-4}$@ 1140 K
20% Ti-$Ca_3Co_4O_9$	22.4	22.3	23.9@ 1140 K	+121	+136	+170 @ 1140 K	$6.6*10^{-5}$	$7.67*10^{-5}$	$1.3*10^{-4}$@ 1140 K
$Ca_3Co_{4-x}Fe_xO_9$	38.7	35.9	19.8@ 1140 K	+122	+139	+159 @ 1140 K	$3.86*10^{-5}$	$5.36*10^{-5}$	$1.27*10^{-4}$@ 1140 K
$Ca_3Co_{4-x}Ni_xO_9$	36.6	31.8	22.8@	+124	+142	+158	$4.17*10^{-5}$	$6.35*10^{-5}$	$1.2*10^{-4}$@

			1140 K			@ 1140 K			1140 K
$La_{0.90}Ca_{0.10}CoO_3$	3	0.71	0.67	+107	+32.2	+12.1	$3.8*10^{-6}$	$1.4*10^{-6}$	$2.1*10^{-5}$
$La_{0.80}Ca_{0.20}CoO_3$	0.64	0.47	0.69	+30	+18.7	+8.9	$1.4*10^{-6}$	$7.4*10^{-5}$	$1.1*10^{-5}$
$LaCo_{0.99}Ti_{0.01}O_3$	280	3	1.04	-220	+45.5	+16.6	$1.28*10^{-5}$	$8.09*10^{-5}$	$3.08*10^{-5}$
$LaCo_{0.90}Ti_{0.10}O_3$	800	30	3	+35	+59	+27.7	10^{-7}	$1.4*10^{-5}$	$2.52*10^{-8}$
$LaCo_{0.80}Ti_{0.20}O_3$	$8*10^{3}$	105	5.2	+200	+120	+38.5	$4*10^{-7}$	$1.4*10^{-5}$	$2.82*10^{-5}$
$LaCo_{0.70}Ti_{0.30}O_3$	$300*10^{3}$	463	264	+530	+253	+63	$7*10^{-8}$	$1.3*10^{-5}$	$3.65*10^{-5}$
$LaCo_{0.60}Ti_{0.40}O_3$	$1*10^{8}$	$38*10^{3}$	394	non	+284	+101	non	$2*10^{-7}$	$3.8*10^{-6}$
$LaCo_{0.50}Ti_{0.50}O_3$	non	$6*10^{7}$	$37.8*10^{3}$	non	+300	+192	non	10^{-9}	$9.7*10^{-8}$
$LaCo_{0.98}Ni_{0.02}O_3$	39.4	1.4	0.85	+336	+48.9	+14	$1.8*10^{-4}$	$9*10^{-5}$	$1.97*10^{-5}$
$LaCo_{0.95}Ni_{0.05}O_3$	22	1.7	1.05	+236	+42.2	+12.7	$2.54*10^{-4}$	$1.04*10^{-4}$	$1.53*10^{-5}$
$LaCo_{0.92}Ni_{0.08}O_3$	9.45	1.5	1.03	+191	+40.6	+10	$3.8*10^{-5}$	$1.1*10^{-5}$	$1.4*10^{-5}$
$LaCo_{0.90}Ni_{0.10}O_3$	6	1.2	0.95	+154	+31.7	+9.72	$3.2*10^{-4}$	$1.05*10^{-4}$	$1.11*10^{-5}$
$LaCo_{0.80}Ni_{0.20}O_3$	3	1.1	1.07	+72.9	+21.1	+4.4	$1.4*10^{-4}$	$3*10^{-5}$	$6*10^{-6}$
$NdCo_{0.95}Ni_{0.05}O_3$	42	5.3	1.1	+282	+103	+20.4	$1.89*10^{-4}$	$1.98*10^{-4}$	$3.6*10^{-5}$
$PrCo_{0.95}Ni_{0.05}O_3$	66	4.5	1.2	+328	+78.7	+21	$1.62*10^{-4}$	$1.36*10^{-4}$	$3.68*10^{-5}$
$SmCo_{0.95}Ni_{0.05}O_3$	97	11	1.34	+315	+158	+24.6	$1*10^{-4}$	$2.15*10^{-4}$	$4.5*10^{-5}$
$GdCo_{0.95}Ni_{0.05}O_3$	285	21.8	1.6	+335	+211	+27.7	$3.9*10^{-5}$	$2.05*10^{-4}$	$4.78*10^{-5}$
$DyCo_{0.95}Ni_{0.05}O_3$	$5.54*10^{3}$	169	7.06	+455	+290	+33.4	$3.7*10^{-6}$	$5*10^{-5}$	$1.58*10^{-5}$

Table. Transport properties of some selected materials

5. Discussion

Functional principal

Thermoelectric power generation is based on the heat and entropy transport of electrons in solids. When a temperature gradient is applied to a solid, electrons (or holes) thermally diffuse from the hot end to the cold end, and carry their charge with them. This charge builds up on the cold end and creates an electric potential known as the Seebeck effect, see Figure 4.

The induced voltage V depends on the temperature difference between hot and cold end and is given by: $V = S\ \Delta T$, where V, is the voltage, S is the Seebeck coefficient and ΔT the temperature gradient.

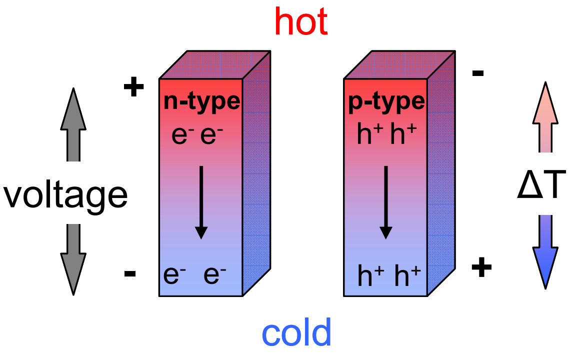

Figure 4. Schematic view of the Seebeck effect.

A thermoelectric generator consists of thermocouples, comprising *p*- and *n*-type thermoelement connected electrically in series and thermally in parallel, see Figure 5. If the hot ends of the n-type and p-type material are electrically connected, and a load connected across the cold ends, the voltage produced by the Seebeck effect will cause current to flow through the load, generating electrical power.

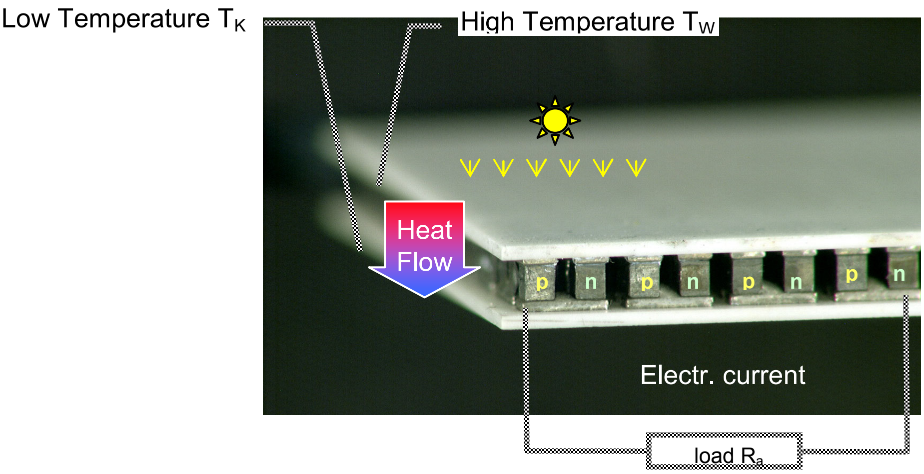

Figure 5: Cascade of thermoelectric *n*- and *p*-type thermocouples. The n-type and p-type materials are connected electrically such that a current I flows

Cobalt oxides have attracted increasing attention for thermoelectric applications owing to the fact that they exhibit semiconducting or metallic electric conductivity, a large Seebeck coefficient, and they are stable at high temperatures in air. Among the oxides, lanthanum cobalt perovskite-type oxides were considered good starting materials for developing potential thermoelements since they can be applied for the p- and the n-type legs of the converter.

The perovskite structure possesses a very high degree of compositional flexibility, being able to tolerate a wide variety of cations on both the A and B sites and thus allowing the fine tuning of physical properties. Low level substitution in the $LaCoO_3$ system considerably improves its transport properties by changing the oxidation state of Co. In addition, large Seebeck coefficient values are preserved.

Steps:

- *Low level substitutions* (Ca, Ni, Ti); this approach increases the electronic conduction and keeps a large Seebeck coefficient.
- *Compositional and structural changes* in materials with high Seebeck coefficient values, e.g. $LaCoO_3$ S ≅ + 600 µV/K.
- *Tuning of the bandwidth of the perovskite structure by changing the size of the Lanthanide*, e.g. in the $LnCoO_3$ and $LnMnO_3$ systems. The perovskite phase will crystallized in different crystal structures depending on the size of the Ln element. As the size of the Ln element and hence the tolerance factor (t) increase, the orthorhombic distortion decrease leading to higher symmetry. By fine-tuning of symmetry we expect to enhance the power factor in the desired temperature range by directly influencing the physical properties of the material, concerning spin-state transitions
- *Introducing elements with high atomic number*, e. g. Lanthanides: Gd, Dy, Er, and Yb, into the perovskite crystal structure. With this approach we expect to reduce the phonon contribution because these elements have smaller phonon energies, lower speed of sound and lower intrinsic thermal conductivity.
- *Nanostructured materials*: This can lead to large improvements in the thermoelectric performance due to quantum confinement of charge carriers and the resulting modification of the band structure. Further improvements are expected due to suppression of the thermal conductivity.
- *Modification of the dimensionality*, lowering may enhance the figure of merit by improving both electronic and lattice properties. Very thin films are expected to increase the efficiency up to 7 times over bulk materials. This approach will be accomplished by growing epitaxial thin film by Pulse Laser Deposition (PLD) and polycrystalline thin films by spin-coating.
- *Characterization of thermoelectric properties at high temperatures*. The Seebeck coefficient, thermal conductivity, and resistivity of the oxides—key parameters to determine the thermoelectric performance of a material—must be investigated and correlated to their morphology, composition, crystallinity, and microstructure.

$LaCoO_3$ system was found to be the best candidate as starting point to develop novel thermoelectric material due to its high Seebeck coefficient value of 600 mV/K at room temperature but the electrical conductivity is high, 10 Ω*cm. The thermoelectric properties in this system can be tuned by suitable Co-site and Ln-site substitution. The substitution of Ca for La in the 3D-compound decrease the electrical resistivity down to a value of 0.1 Ω cm for x = 0.40. This dramatically decrease of the electrical resistivity is associated to an increase of Co^{4+} and thus the number of holes in the mixed valance band. The Co^{4+} formation is induced through substitution of the La^{3+} by Ca^{2+}. The value of the thermopower of the Ca-substituted $LaCoO_3$ is ≈ 70 µV/K at 300 K. The power factor has a value of 4.9 * 10^{-6} W / K^2 m at room temperature. To further reduce the electrical resistivity and increase the power factor, we have studied the influence of low level Ca and Ti substitution in the $LaCoO_3$. In the $La_{0.90}Ca_{0.10}CoO_3$, the effect of 0.01% of Ti doping produced a reduction of 20% in the Seebeck coefficient value (from 184 µV/K to 146 µV/K) caused probably due to the creation of both types of carriers (electrons and holes). In order to have compounds with semiconducting-like behaviour and keep high Seebeck coefficient values we study the low level substitution of Co by Ni and Ti. We found that small amount of Ni significantly decreases the electrical resistivity, e.g. 2% Ni ions in the cobaltate structure reduces the electrical resistivity to a value of 39.40 mΩ*cm at 345 K. On the other hand, in the low substitution region the Seebeck coefficient remains high, e.g. for X = 0.02 we obtain $S_{exp(300K)}$ = 360 µV/K. In this region where the conduction is by hopping mechanism, the temperature-independent thermoelectric power can be described by Heikes formula [3], $S = -(k_B/ e) Ln(x / 1-x)$, where *x* is the carrier concentration. Applying this formula e.g. for x = 0.02 we obtain S_{Heikes} ~350 µV/K which is in good agreement with our experimental value, $S_{exp(300K)}$ = 360 µV/K, and for x = 0.10 we obtain S_{Heikes} ~200 µV/K which agree with $S_{exp(300K)}$ = 173 µV/K at room temperature. For higher Ni content where the $LaCo_{1-x}Ni_xO_{3-\delta}$ becomes metallic, the Seebeck coefficient does not follow Heikes equation. The thermoelectric power factor at room temperature was enhanced to 2.7*10^{-4} W / K^2 m for sample with 10% Ni content, which is two orders of magnitude higher than the non-substituted $LaCoO_3$ compound, PF = 3.6 * 10^{-6} W / K^2 m. We observed an increases of the electrical resistivity with increasing Ti content. The power factor, PF, for the Ni substituted samples is PF = 1.42*10^{-4} W/m^2*K for x = 0.10 at T = 540 K and decreases with temperature. The $LaCo_{1-x}Ti_xO_{3\pm\delta}$ compounds reveal an enhancement of the power factor with increasing temperature. Ti substitution leads to a higher power factor compared to that of Ni substitution at T = 1240 K.

We have also studied the effect of Ln substitution on thermoelectric properties of the LnCo0.95Ni0.05O3-□ system (Ln = La, Pr, Nd, Sm, Gd and Dy). The variation of the lanthanide ionic radii influences the crystal structure. While the LaCo0.95Ni0.05O3-□ crystallizes in rhombohedral system, the parent compounds with smaller rare-earth cations crystallized in orthorhombic system. These structural changes involves modifications on the electronic band structure and therefore on the thermoelectric properties of the LnCo0.95Ni0.05O3-□ system, e.g. the temperature of the semiconductor to metal transition is increasing with decreasing rare-earth ionic radii.

A good thermoelectric material has to exhibit a high power factor but low thermal conductivity. Taking into account that S, σ and κ are interdependent- changing one alters the others, making the optimization extremely difficult. Our challenge for the materials design is to reduce thermal conductivity and therefore enhance the figure of merit, Z, without affecting the power factor using nano-scale materials. The thermal conductivity in metal oxides is predominantly due to optical phonons and the total thermal conductivity has values around 2.5 W/Km at room temperature. Submicrocrystalline cobaltate particles with perovskite structure are prepared by soft chemistry methods based on the chelation of metals by citric acid in aqueous solution, see above. The heat conduction is lowered by reducing the particle size to a submicrometer level. Assuming that the phonon is the predominant carrier of the heat conduction, the lattice thermal conductivity is reduced by boundary scattering without affecting electrical transport. The thermal conductivity for all samples is low (1.5 W/mK $< k < 2.5$ W/mK up to 1200K) resulting in an enhancement of the thermoelectric figure of merit. Since dimensionality is an important parameter to modify heat conductivity and therefore the figure of merit, we have interested the “Misfit cobaltites family” (layered compound) due to their promising properties for thermoelectric applications as a result of their structure. The measured thermoelectric values measured on the nanostructured “misfit cobaltite”, $[Ca_2CoO_3]^{RS}$ CoO_2, showed a Seebeck coefficient of 120 µV / K and an electrical resistivity of 9.7 mΩ cm at 335 K. Thus the power factor has a value of $1.48\ 10^{-4}$ W / K^2 m and increases with increasing temperature. Polycrystalline films produced by spin-coating and single crystalline films produced by PLD are being evaluated.

6. Conclusions

Perovskite-type oxides are promising new thermoelectrics for high temperature applications, but further studies on this brand new functional materials are required to understand the composition-structure-properties relations which is a prerequisite for the thermopower tuning.

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