

# PEROVSKITE-TYPE THERMOELECTRIC OXIDES AND OXYNITRIDES

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## Abstract

Direct and efficient thermoelectric conversion of solar or geothermal waste heat into electricity requires the development of *p*- and *n*-type thermoelectrics with similar materials properties. Perovskite-type transition metal-oxides and oxynitrides are investigated 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.

Cobaltates, ferrates and nickelates with *p*-type conductivity and *n*-type titanates, molybdates and manganates are considered for the development of an ceramic thermoelectric converter. Nitridation of perovskite-type titanates and molybdates offers an alternative route to control the carrier concentration, band structure and mobility of charge carriers of the compounds which leads to further possibilities to tune the thermoelectric properties.

## Introduction

The conversion efficiency of a thermoelectric converter depends strongly on the applied materials and their Figure of Merit,  $Z = S^2/\rho\kappa$ . The direct conversion of the heat flux into electricity is connected to electron transport phenomena, and the interrelated Seebeck effect. With the discovery of large thermopower in metallic  $\text{Na}_y\text{Co}_2\text{O}_4$  [1], complex metal oxides have been recognized as good candidates to compete with conventional materials for

thermoelectric power applications [2]. In complex transition metal oxides the spin of electrons can become an additional source of entropy resulting in the large thermopower in these systems [3]. Complex transition metal oxides are widely used for energy conversion processes. They crystallize in specific structural types characterized by the coordination geometry of metal-anions polyhedra, which are determining their chemical and physical properties. Perovskite phases are complex metal oxides with the general formula  $ABX_3$ . Here the *B* cations in this crystallographic structure form a 3D-framework of corner-sharing coordination octahedra with the anions. The slightly larger *A* cation can be found inside the cub-octahedral cavity formed by eight corner sharing  $BO_6$  octahedra (see Figure 1)

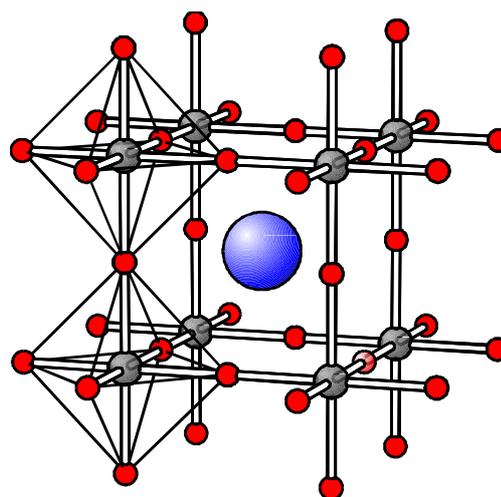


Figure 1: Schematic representation of the ideal perovskite structure with *B* cations (grey) surrounded by six anions (red) forming the coordination octahedron. The *A* cation (blue) is located in the center of eight octahedra.

The amount of charge carriers and thus the electrical conductivity and thermoelectric properties in this system can be tuned by suitable substitution reactions.

The heat transfer in solids is governed by the lattice contribution (phonon vibrations) and the electronic component corresponding to the electron motions. For oxides the phonon contribution remains the predominant component of the total thermal conductivity. Strategies to lower the lattice heat conduction, i.e. enhance the phonon scattering include the application of nanostructures [4]. The interface scattering of phonons can dominate the heat conduction in oxide nanostructures.

In addition to cationic substitutions and introduction of defects into the oxygen sublattice, the exchange of oxygen by other anions such as halides or nitrides can be used to influence the properties of the perovskite-type compounds significantly. Therefore an oxygen- nitrogen exchange in perovskite-type oxides was performed with an ammonolysis reaction.

## Experimental

Perovskite-type oxides with diverse composition were produced by a chimie douce synthesis process. Powders of the Ca- and Ni-substituted substituted Lacobaltates and manganates were synthesised with diverse precursor reactions. The precursors were obtained by dissolving the required amount of  $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$  (Merck,  $\geq 97\%$ ),  $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck,  $\geq 99\%$ ),  $\text{Ca}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck,  $\geq 97\%$ )  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck,  $\geq 97\%$ ) and  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck,  $\geq 97\%$ ) etc. in water and mixing them with a chelating agent, e.g. citric acid. These complexes were polymerised in a second step and dried to obtain homogeneous aerogel precursors. The ammonolysis was conducted in either thermal reactions or in a plasma enhanced chemical reaction using a microwave induced ammonia plasma

reactor. The thermal ammonolysis reaction was performed at temperatures of  $900^\circ\text{C} < T < 1000^\circ\text{C}$  in a rotating cavity reactor using a dry ammonia flow of 10 mL/min. A self made microwave induced ammonia plasma (MIAP) reactor was used for the plasma reactions. Phase purity of the products was confirmed by X-Ray Diffraction (XRD) with a PANalytical X'pert diffractometer using  $\text{Cu-K}\alpha$  radiation. The morphology of the calcined powders was studied using a Scanning Electron Microscope (SEM) LEO JSM-6300F with EDX detector. The structure of the samples was further studied by Transmission Electron Microscopy (TEM) using a Philips CM 30. Neutron powder diffraction data were recorded on the High Resolution Powder Diffractometer for Thermal Neutrons (HRPT) of the Swiss Neutron Spallation Source SINQ at the Paul-Scherrer-Institute (PSI) in Switzerland. Data collection at room temperature and 1.5 K-200 K were performed in the high intensity modus of the instrument. Rietveld refinements were performed with FULLPROF 2000 [5] software. The oxygen content of the powders was determined by the hot gas extraction method using a LECO TC 500. The transport properties measurements were performed on bar shaped pressed-sintered pellets with general dimensions of 1.65 mm \* 5 mm \* 1 mm. The electrical conductivity and Seebeck coefficient were measured in air simultaneously as a function of temperature from 340 K to 1273 K using a RZ2001i measurement system from Ozawa Science, Japan. The electrical conductivity was determined using a four-point probe method. Two electrical contacts were positioned at both ends of the sample and the two others contacts were on the sample body. Circular pellets (10mm diameter) of the same composition were used for thermal conductivity measurements by the laser flash method using a Netzsch LFA-457 apparatus from 300 K to 1020 K in argon atmosphere.

p- and n-type legs are produced with the obtained samples and assembled to all perovskite ceramic thermoelectric converters.

## Results

Among a wide range of potential perovskite-type candidates with positive and negative thermopower for thermoelectric applications we selected semiconducting cobaltates, titanates and manganates values (see figure 2) to study possibilities for improving the figure of merit  $ZT = S^2T/\rho\kappa$  by enhancing the electrical conductivity and the Seebeck coefficient with appropriate cationic substitutions and by lowering the heat conductivity with decreasing the particle size [6-8].

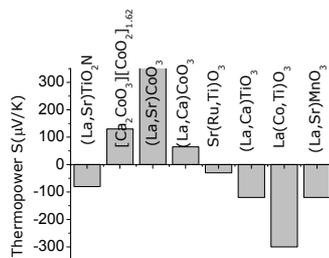


Figure 2: Many perovskite-type phases show a high thermoelectric activity with positive Seebeck coefficient as well as negative Seebeck coefficient.

A series of A and B-site substituted lanthanum cobaltate, manganate and molybdate compounds with various compositions and perovskite structure have been successfully synthesised by the polymeric precursor method [9]. All samples are single phase and crystallize in perovskite-type crystal structure.

The thermal conductivity can be reduced by lowering the particle dimensions to the nanometer scale with a *chimie douce* synthesis method (see figure 3).

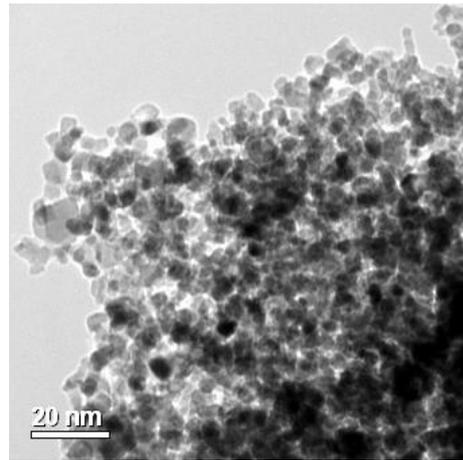


Figure 3: TEM view of lanthanum titanate particles produced by a *chimie douce* method.

The electrical resistivity generally decreases with increasing temperature, representing a semiconducting-like behaviour ( $dp/dT < 0$ ). With the appropriate substitutions the conduction mechanism of Lanthanum cobaltates can be changed from *p*-type semiconductors to *n*-type semiconductors, i.e. electron conduction mechanism to hole conduction mechanism respectively. Substitution of trivalent La cations on the *A*-site position with tetravalent cations (e.g. Ce<sup>4+</sup>) or substitution in the *B*-site Co<sup>3+</sup> matrix with tetravalent cations (e.g. Ti<sup>4+</sup>) produces mixed valence states of Co<sup>3+</sup> and Co<sup>2+</sup>. The Seebeck coefficient of the manganates and nitrogen doped titanates is negative.

## Conclusions

Perovskite-type cobaltate, manganate and titanate thermoelectrics were successfully synthesised and characterised. The electrical conductivity, the Seebeck coefficient and the thermal conductivity were measured in a broad temperature range. The studied perovskite-type phases show potential for thermoelectric applications, as the thermopower relies on the tuneable itinerant charge carriers. The sign and the absolute value of the Seebeck coefficient can be changed with hole or electron doping. By combining suitable p-

and n- type materials perovskite-type thermoelectric converters can be produced.

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