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Geo-Thermopower (Geo-TEP) – Materials

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ZUSAMMENFASSUNG

Die Nutzung von Geothermie als alternative Energiequelle ist eine ökologisch und ökonomisch attraktive Lösung zunehmender Energieproblematik. Eine effiziente thermoelektrische Umwandlung im niederen Temperaturbereich (T_w < 400K) in Elektrizität erfordert die Entwicklung neuer Funktionsmaterialien, die einen grossen Seebeck Koeffizienten, gute elektrische Leitfähigkeit, sowie geringe Wärmeleitfähigkeit aufweisen. Da gute elektrische Leitfähigkeit meistens mit einer guten Wärmeleitfähigkeit einhergeht, ist die Entwicklung eines geeigneten Materials eine große Herausforderung.

Übergangsmetalloxide mit perowskitartigen Strukturen können sowohl p- als auch n-leitende Halbleiter sein, die zum Teil eine grosse Thermokraft aufweisen. Ihre sehr gute thermische Stabilität in Luft, welche durch thermogravimetrische Experimente verifiziert wurde, zeigt dass diese Substanzen für thermoelektrische Anwendungen hervorragend geeignet sind. Die Thermokraft und andere Transport- Eigenschaften dieser Keramiken werden durch geeignete Änderung der Zusammensetzung und Morphologie gezielt beeinflusst.

In den ersten 3 Monaten des laufenden Projektes wurden innovative Synthesemethoden für die Darstellung von feinkristallinen Pulvern entwickelt. Die Charakterisierung der Proben erfolgt mittels Pulver-Röntgendiffraktion, Elektronenmikroskopie, und volumetrische Adsorptionsanalytik (BET-Methode). Elektrischer Widerstand und Thermokraft der Proben wurden in einer an der Empa entwickelten Apparatur bestimmt. Die thermischen Eigenschaften, wie z.B. Wärmekapazität wurden in thermoanalytischen Experimenten ermittelt.

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Projektziele

The use of geothermal or waste heat as energy source is an attractive and environmentally clean way to generate electrical power. With thermoelectric devices, heat can be directly converted into electricity at all geothermal temperature levels. The amount of electrical power produced is depending on the thermoelectric conversion efficiency of the device and the heat flux [1]. To enhance the conversion efficiency highly efficient new thermoelectric materials exhibiting low heat conductivity, small resistivity, and large Seebeck coefficients have to be identified.

Novel thermoelectric materials with p-type conductivity as well as compounds with n-type conductivity for cascades of Thermoelectric devices will be developed to convert the applied temperature gradient of geothermal heat exchanger systems into electric power. In these devices several couples of p- and n-type-legs are connected electrically in series and thermally in parallel to produce an open circuit voltage of several volts at even low temperature gradients (see figure 1).

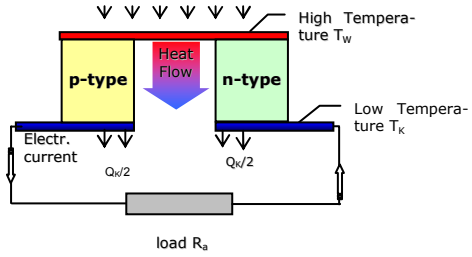


Figure 1: Schematic of a single-couple thermoelectric converter consisting of a p- and n-type semiconductor leg

Low values of the thermal conductivity allow to retain heat at the junctions and to maintain a large temperature gradient. The optimization of thermoelectric properties via a low thermal conduction requires a decrease of the phonon contribution. Complex crystal structures, heavy element substitutions, solid solutions and reduction of the grain size [2] can lower the thermal conduction by the reduction of the phonon contribution. Many perovskite-type oxides exhibit promising properties for thermoelectric applications. With this flexible crystallographic structure p- and n-type semiconductors can be obtained with suitable substitutions. Perovskite-type phases with various compositions are produced using a *chimie douce* method [3]. This low temperature synthesis process supports the production of ultrafine single-phase particles.

Durchgeführte Arbeiten und erreichte Ergebnisse

Perovskite-type transition metal oxides are synthesized by the cationic complexation technique. The mentioned *chimie douce* method is based on the chelation of metals by citric acid in aqueous solution. Fine powders are obtained by thermal decomposition of the corresponding amorphous citrate precursor. $LaCo_{1-X}Ni_XO_{3-d}$ (with $0.02 \leq x \leq 0.3$) perovskite phases have been successfully synthesized by the chimie douce method. All phases are thermoelectrically active and show power factors up to $3.7*10^{-4}$ mV/K^2cm [4].

The thermal decomposition of the citrate precursor is studied by thermogravimetric analysis coupled with a mass spectrometer. Related infra-red spectroscopy was performed to understand the decomposition mechanism.

1. Citrate precursor decomposition

The thermogravimetric analysis of the citrate precursor powder revealed a decomposition mechanism and appropriate synthesis temperatures (see Figure 2). The decomposition in synthetic air can be divided in different thermal events.

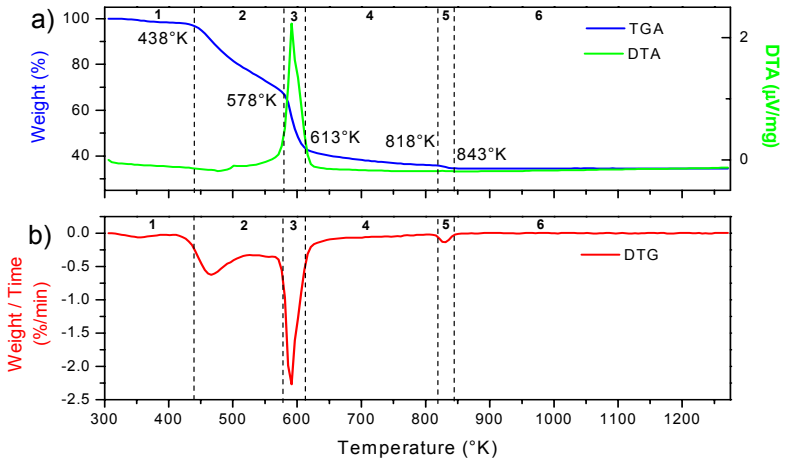


Figure 2 (a): TGA / DTA curves and Figure 1 (b): DTG curve (in synthetic air: 80% He and 20% O_2, 2°C/min) of La-Co-Ni citrate precursors (predried at 423°K)

Below 438 K, a weak endothermic peak with a release of water (m/z 18) is observed (see Figure 2b). A water desorption of the (La, Co, Ni)-citrate citrate xerogel occurs in this first temperature region.

A reorganisation of the organic matrix during the second step (438 K < T < 578 K) is accompanied by a loss of citric acid fragments: $C_3H_3^+$ (m/z 39), $C_2H_2O_2^+$ (m/z 58) and $C_4H_4O^+$ (see Figure 2a). This molecular rearrangement is also observed under inert atmosphere (not shown). Under inert or oxidising atmosphere, the release of CO_2 (m/z 44) (see Figure 3b) is observed. The emission of CO_2 occurs due to the decomposition of the citrate precursor and not as a result of a combustion process.

The third temperature region (between 578 K and 613 K) is defined by a strong exothermic event which is related to the release of H_2O and CO_2. In this temperature region, the presence of carbonate ions is detected by infra-red data (not shown). Intermediate phases (as oxycarbonate) are probably formed during this oxidation step.

Above 818 K, a small exothermic event is accompanied by a release of CO_2. A decarbonisation of the product leads to the desired pure perovskite phase around 873 K. The thermal stability is confirmed by thermogravimetric analyses up to 1273 K.

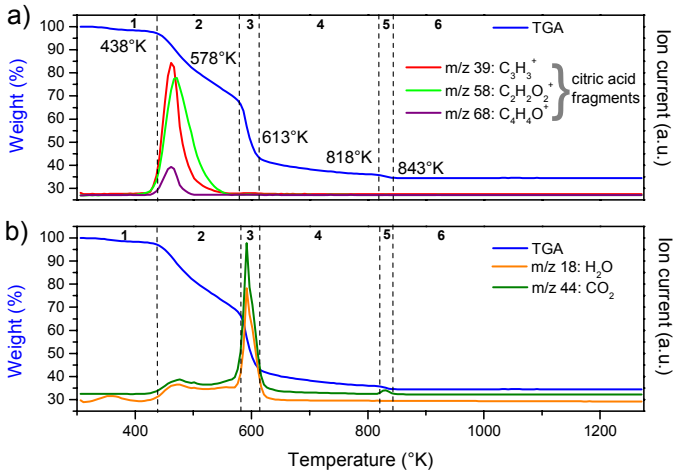


Figure 3: TGA and MS signals (in synthetic air: 80% He and 20%O_2, 2 K/min) of precursors (predried at 423 K).

Figure 3 (a) MS plots: m/z 39: $C_3H_3^+$, m/z 46: NO_2, m/z 58: $C_2H_2O_2^+$, m/z 68: $C_4H_4O^+$ (enlarged).

Figure 3 (b) MS plots: m/z: 18 H_2O, m/z 44: CO_2.

2. Phase formation

The crystallisation process starts at about 823 K. At T > 843 K, the perovskite phase is formed and stable; no weight loss was detected at higher temperature. The perovskite crystallinity improve further thermal treatment (see Figure 4).

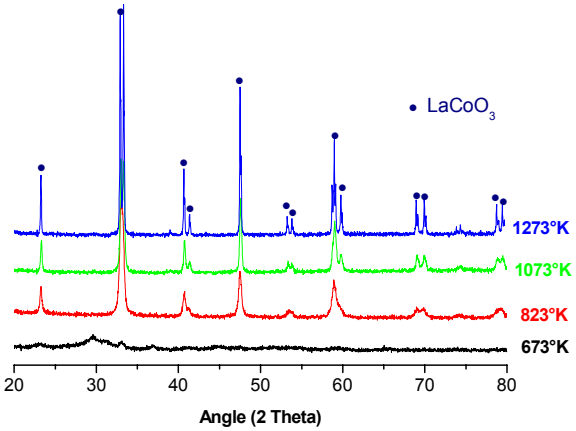
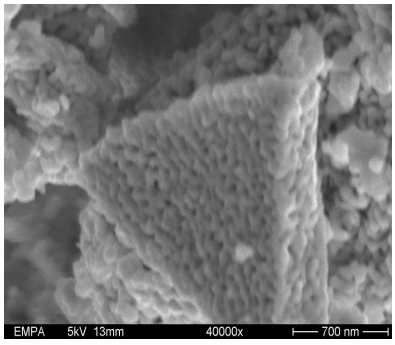


Figure 4: X-Ray Diffractograms after calcination in air at different temperatures for 4h.

3. Influence on the morphology

The spherical particles have a uniform particle size. The powder appears partly agglomerated with tiny pores due to the gas evolution (see Figure 5). The powder shows a particle diameter of approximately 50nm at 823 K.

A further particle growth can be observed after applying a thermal treatment (Figure 5 and 6). A better control of the particle size is possible if the particle agglomeration is controlled in aerosol processes, i.e. the precursor decomposition is performed inside micro-droplets using ultrasonic spray combustion (USC) [5].



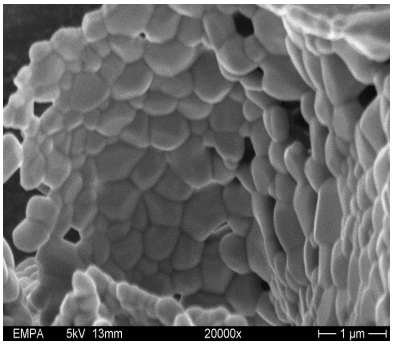


Figure 5 and 6: SEM micrograph pictures of $LaCo_{0,95}Ni_{0,05}O_3$ prepared at 873°K and 1273°K.

4. Heat capacity measurements

One important parameter to determine the thermal conductivity is the heat capacity. The evolution of the heat capacity as a function of the applied temperature has been determined for different low level doping samples [6].

The temperature dependence of the specific heat capacity has been investigated on the nickel doped lanthanum cobaltates. The evolution of the specific heat capacity of different compositions of nickel doped lanthanum cobalt oxides (5%, 15% and 25% of nickel) has been studied between 300°C and 1000°C, by Differential Scanning Calorimetry (three step procedure). All the compositions show very similar specific heat capacity values, between 0.4 and 0.7 J g^{-1} K^{-1} (see Figure 7). The 25% of nickel doped gives the lowest specific heat capacity.

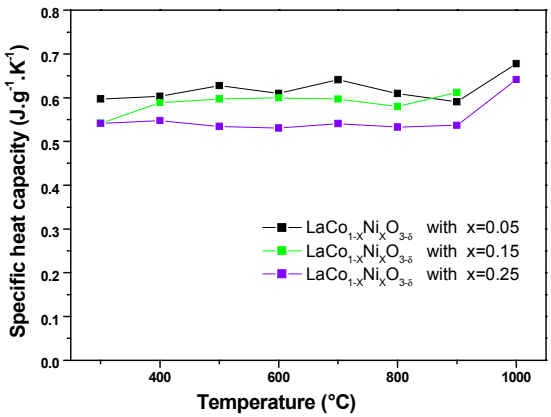


Figure 7: Evolution of the specific heat capacity of $LaCo_{1-x}Ni_xO_{3-\delta}$ (with x=0.05; 0.15 and 0.25) as a function of temperature.

Nationale Zusammenarbeit

Close collaborations exist with the project partners at ETHZ:

- Klaus Fröhlich, Electric Power Transmission and High Voltage Technology Laboratory, ETHZ: System design packaging of the thermoelectric module. Modeling und simulation of the coupled thermal and electric systems including irreversibilities (project: Das thermoelektrische Kraftwerk).
- Aldo Steinfeld and Dimos Poulikakos, Institute of Energy Technology, ETHZ &PSI: Design and optimization of the heat exchange devices; fundamental analysis of the heat transport mechanism for transferring efficiently low-temperature geothermal energy to the electrical converter.

Internationale Zusammenarbeit

- SAM – Span und Mayrhofer KEG, A-6112 Wattens: Production of a thermoelectric demo device.

Bewertung 2005 und Ausblick 2006

During these first 3 months of the PhD thesis project various thermoelectric active materials could be successfully produced and characterised concerning thermoelectric and structural properties.

It was shown that the thermal properties, i.e. the phonon transport can be influenced by changing the morphology and composition of the materials. With a particle size smaller than the mean free path of the phonons the thermal conductivity of the semiconductors was lowered by factor 5.

The first results of the project were already presented in three conference contributions by the PhD student [5-7].

For the next funding period a screening for alternative low cost and highly efficient thermoelectric materials with p- and n-type semiconductor properties are planned. Furthermore low temperature synthesis processes for high surface area intermetallic compounds are envisaged.

Empa is planning major hardware investments. Thus a novel high temperature Seebeck and electrical conductivity measurement system from Ozawa Science for measurements up to 1200 K will be installed which will be the first set-up of this kind in Europe.

Additionally a laser flash thermal conductivity measurement system is evaluated to be installed at Empa beginning of next year. This apparatus will be the first in Switzerland.

Referenzen

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[3] A. Weidenkaff, Preparation and application of nanoscopic perovskite phases (invited review), *Adv. Eng. Mat.*, **6** 709, 2004.

[4] Robert, R., Bocher, L., Balasz, S., Döbeli, M. and A. Weidenkaff, *Progr. in Solid State Chem.*, accepted for publication.

[5] L. Bocher, R. Robert, P. Hug, M. Trottmann, and A. Weidenkaff, Thermal properties of nickel doped cobaltate phases (poster), 1st Empa Symposium for Ph.D. students, Dübendorf, Switzerland, 20th October 2005.

[6] L. Bocher, Thermal investigations on complex transition metal oxides (oral presentation), 2nd Empa – PSI PhD students day, Villigen, Switzerland, 2nd December 2005.

[7] L. Bocher, C. Schreiner, M. Trottmann, D. Logvinovich, R. Robert, P. Hug and A. Weidenkaff, Chimie douce synthesis methods for perovskite-type cobaltate, titanate and manganate phases with variable compositions (poster), International Conference on Perovskites - Properties and Potential Applications, Sept 5-8, 2005.