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TOM

ERSTELLEN UND MODELLIERUNG EINES THERMO-ELEKTRISCHEN OXIDISCHEN MODULS (TOM) ALS DEMONSTRATOR

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ZUSAMMENFASSUNG

Four-leg oxide thermoelectric modules have been produced by combining *p*-and *n*-type oxide elements made of $GdCo_{0.95}Ni_{0.05}O_3$ and $CaMn_{0.98}Nb_{0.02}O_3$ respectively. The modules were assembled using a mixture of silver paste, powders of silver and copper oxide. The legs were inserted alternately between the alumina plates.

The cross-sectional preparation of Ag mixture/alumina substrate was analysed by SEM. The thermoelectric performance of a module was investigated up to a maximum temperature 835 K with temperature differences of up to 773 K between the hot and cold side of the module. For the temperature distribution measurement, a dedicated micro - IR camera was used.

Thermal stability and electrical resistivity of the contacts are considered with regard to the thermal expansion between the oxide legs and the Ag contact. Furthermore the maximum power output, P-V characteristics, manufacturing quality factor and conversion efficiency are evaluated for different temperature differences and different thermoelectric length legs.

New oxide materials were synthesised by soft chemistry methods and will be tested in the future as *p*-type element for the next generation of oxide thermoelectric modules. A promising power factor of 1.10^{-4} $W.m^{-1}.K^{-2}$ was obtained at 1300 K for $La_{0.8}Gd_{0.2}FeO_3$.

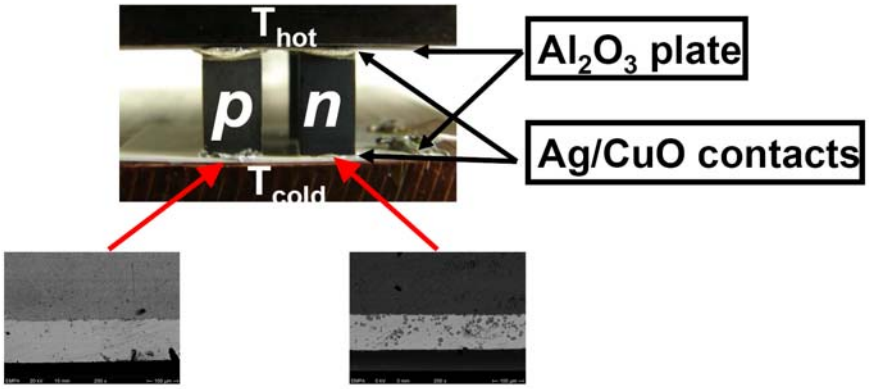
Projektziele

Thermoelectric materials are candidates for devices, which can directly convert heat into electrical energy. The energy conversion efficiency of thermoelectric materials is evaluated using the figure of merit, Z, defined as $Z = \sigma S^2 \kappa^{-1}$ (σ is the electrical conductivity, S is the Seebeck coefficient and κ is the thermal conductivity). Oxide ceramics are most promising potential candidates as thermoelectric materials because they are relatively stable at high-temperature. Thermoelectric properties and doping effects will be investigated in this work.

Durchgeführte Arbeiten und erreichte Ergebnisse

1) Properties of thermoelectric oxide module (TOM)

Three types of thermoelectric oxide modules with different thermoelement length legs were mounted. In this type of module, *p*- and *n*-type semiconductor thermoelements are connected electrically in series by highly conducting metal strips from silver with CuO and sandwiched between thermally conducting but electrically insulating plates from corundum (Figure 1). For the *p*- and *n*-type legs $GdCo_{0.95}Ni_{0.05}O_3$ (*p*) [1] and $CaMn_{0.98}Nb_{0.02}O_3$ (*n*) were used. The cross-sectional view of the *p*/*n* material-Ag/CuO contact-Al_2O_3 plate is in Figure 1.



Fifure 1: Thermoelectric oxide module and SEM picture for *p*- and *n*-type material.

Thermoelectric modules with different legs-length 10, 5 and 2 mm were measured in order to find the best generator' s performance. Power/Voltage characteristics together with IR-camera pictures are in Figure 2. The best value of power maximum was obtained for 2 mm legs. Nevertheless, from IR-measurement an overheating due to :i) convection along the legs and ii) small temperature gradient can be deduced, since the temperature gradient between the hot and the cold side decreased with decreasing thermoelement length. Figure 3 display the conversion efficiency as a function of temperature gradient end leg length together with maximum power output as a function as a function of temperature difference for modules with cross-sectional area of 4 X 4 mm^2. Conversion efficiency and power output depend on the temperature difference, contact parameters, ZT factor of thermocouple materials (Seebeck coefficient, electrical and thermal conductivity) and the module geometry. It can be seen that the maximum power output increases exponentially with an increasing temperature difference. The conversion efficiency is increasing with a larger temperature difference and/or increasing thermoelement length and was found to be the highest for ΔT = 500 °C (Figure 3b).

The manufacture quality factor (MQF), calculated from the resulting data, determines the performance of a module, having thermoelements with a fixed geometry, fabricated from a given materials and operated in a given temperature regime. In Figure 4 the manufacture quality factor is plotted as a function of the thermoelement length. It can be seen that better values of MQF result with increasing thermoelements length. Thus, a compromise between lowering the length of the device for enhancing the maximum power output value und the MQF enhancement in larger converters have to be realised.

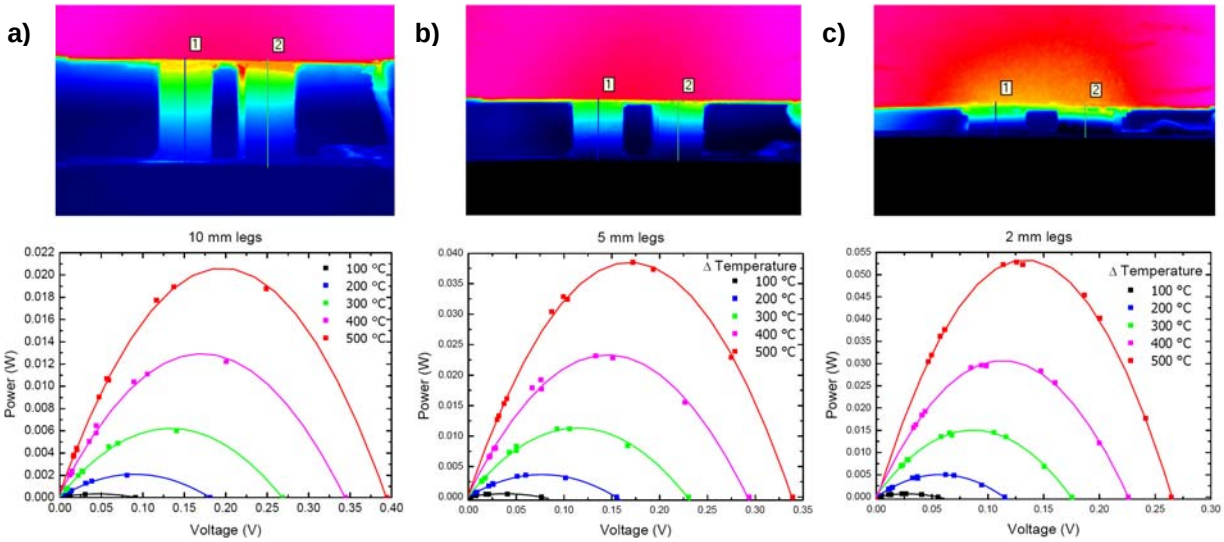


Figure 2: Power output versus voltage at different temperatures together with IR-measurement of distribution heat along the 2 mm legs (a), 5 mm legs (b) and 10 mm legs (c).

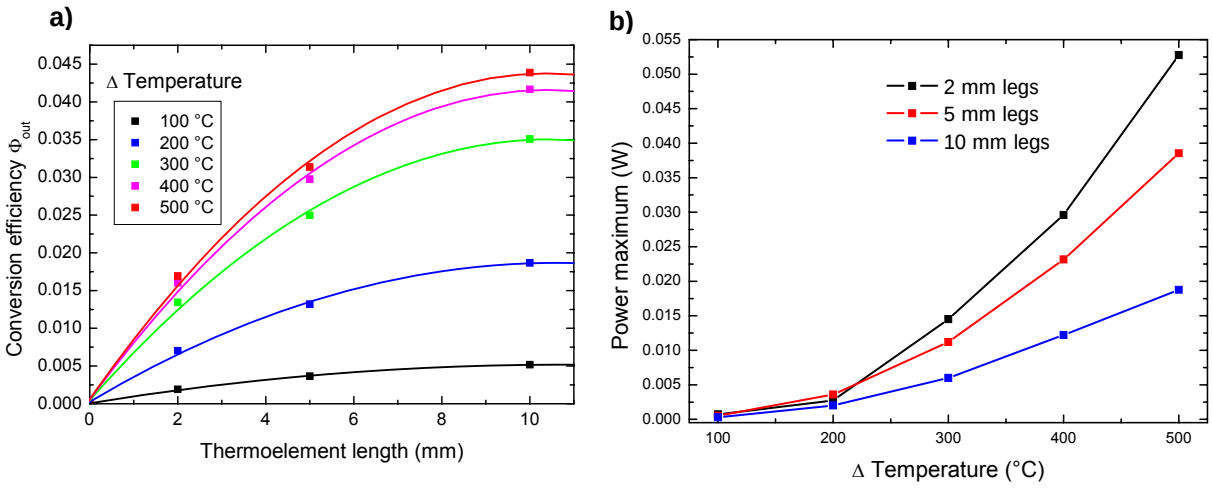


Figure 3: Conversion efficiency as a function of temperature gradient and leg length (a) and maximum power output of thermoelectric oxide modules (b).

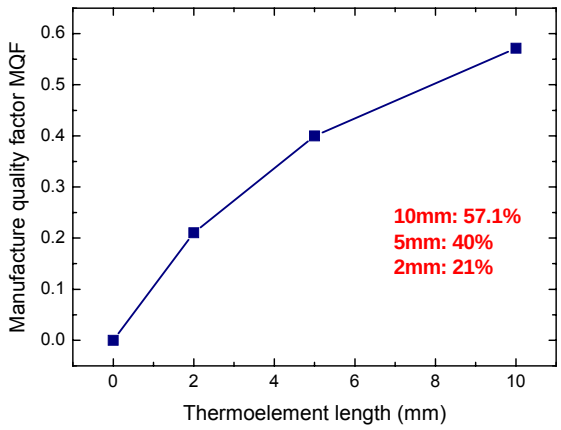


Figure 4: Manufacture quality factor (MF) as function of the leg length.

2) Soft chemistry synthesis and morphology of the samples

Polycrystalline samples of ferrates-perovskite were prepared by soft chemistry [2]. A concentrated solution of metal nitrates precursors was mixed with an aqueous solution of citric acid with following stirring at 353 K to polymerized the solution. Water was evaporated from the mixed solution at 373K until a viscous gel was obtained. The gel was heated overnight at 573 K to yield a powder material which was ground, calcined at 1173 K twice for 12 h. Finally this powder was pressed into a form of pellets and sintered up to 1513 K. All the procedure is in Figure 5.

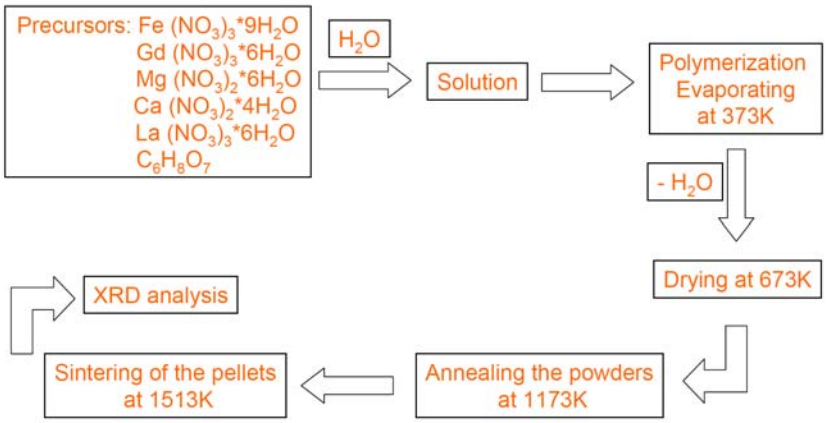


Figure 5: Soft chemistry synthesis method.

By soft chemistry several compounds on the basis $LaFeO_3$ perovskite with dopping of gadolinium, calcium and magnesium were prepared. The sintering temperature to obtain relative high density of the sample was optimised. To compare the morphology and grain size of the sample several SEM studies were performed for the compound $LaFe_{0.8}Mg_{0.2}O_3$ (Figure 6) It is evident that at high temperature the grains are better connected, but the grain size remains almost the same.

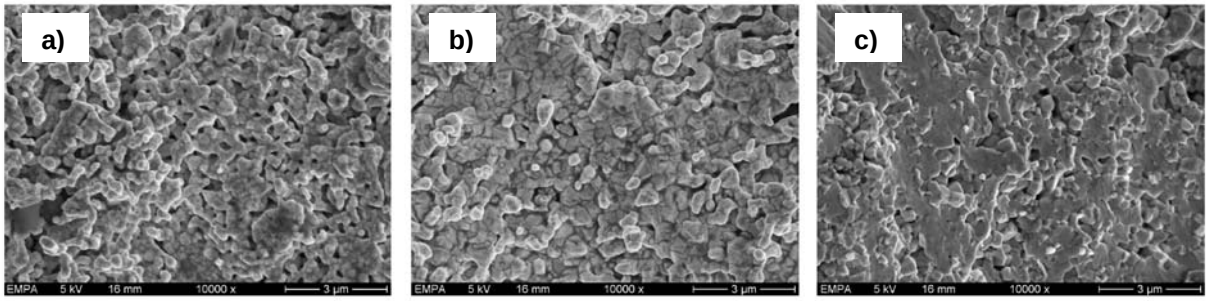


Figure 6: SEM micrograph pictures of the $LaFe_{0.8}Mg_{0.2}O_3$ prepared at 1323 K (a), 1373 K (b) and 1513 K (c).

Influence on the grain size has the content of dopping element. On the Figure 7 there are SEM pictures for the system $LaFe_{1-x}Mg_xO_3$ with x = 0.2, 0.15, 0.1 and 0.05 and size of the grains is increasing with decreasing the content of magnesium.

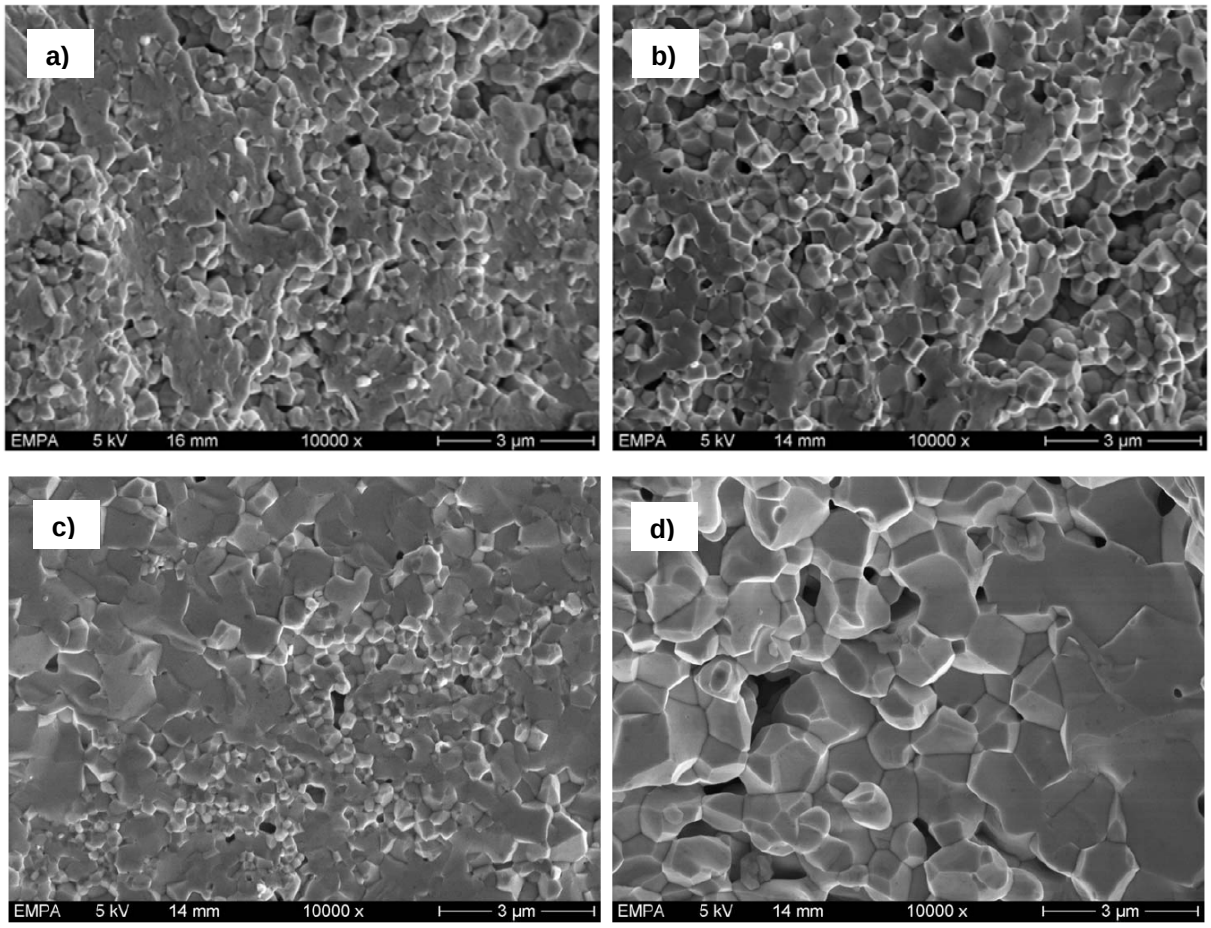


Figure 7: SEM micrograph pictures of the $LaFe_{1-x}Mg_xO_3$ system for x = 0.2 (a), 0.15 (b), 0.1 (c) and 0.05 (d) prepared at 1513 K.

3) Thermal and electrical transport

The electrical resistivity, Seebeck coefficient, and power factor of perovskite-type $La_{0.8}Ca_{0.2}FeO_3$, $La_{0.8}Gd_{0.2}FeO_3$ and $LaFe_{1-x}Mg_xO_3$ (x = 0.05 – 0.2) were investigated in the temperature range of 300 – 1250K to explore their possibility as thermoelectric materials (Figures 8-9). The electrical resistivity of the samples decreases with increasing temperature corresponding to semiconducting behaviour, with the lowest electrical resistivity for the $La_{0.8}Gd_{0.2}FeO_3$. At higher temperature the samples start to become more metallic, i.e. with increasing temperature the electrical resistivity increases. The activation energies were calculated to be up to 1000 meV dependent on the composition. The Seebeck coefficient has a positive character in the whole temperature range indicating predominant hole carrier. At higher temperatures (above about 600 K) the Seebeck coefficient is temperature independent. Thus, this behaviour can be described by the Heikes formula. To discuss the transport properties in the context of thermoelectric application, the figure 8 shows a plot of the thermoelectric power factor as a function of temperature with the highest value 9.12E-5 $WK^{-2}m^{-1}$ at 1245 K for the sample $La_{0.8}Gd_{0.2}FeO_3$.

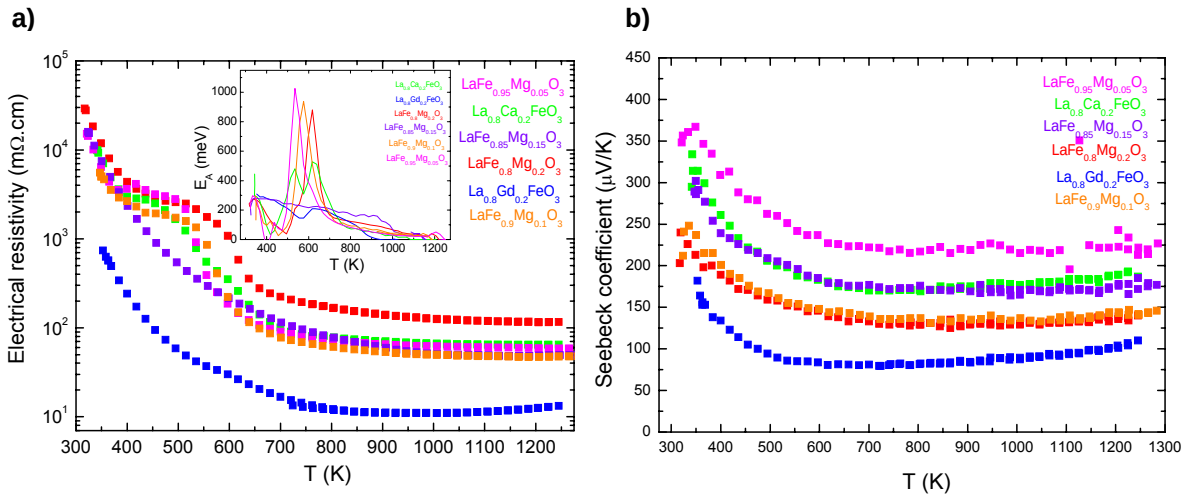


Figure 8: Temperature dependence of the electrical resistivity with the inset of activation energy (a) and temperature dependence of the Seebeck coefficient (b) for the $La_{0.8}Ca_{0.2}FeO_3$, $La_{0.8}Gd_{0.2}FeO_3$ and $LaFe_{1-x}Mg_xO_3$ (x = 0.05 – 0.2).

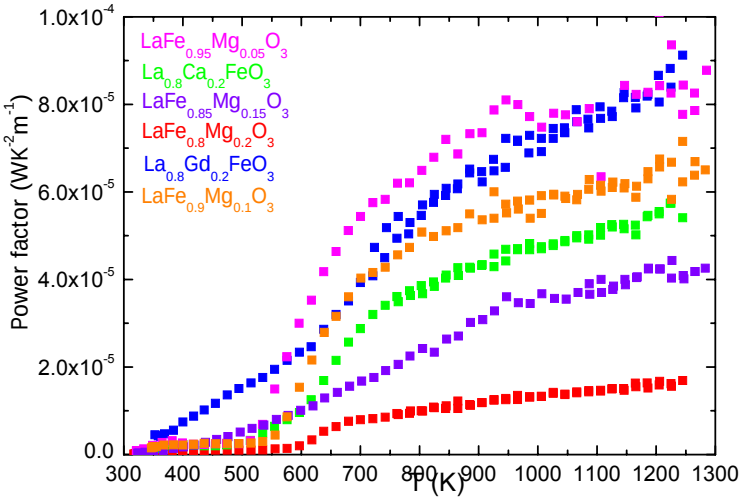


Figure 9: Temperature dependence of the power factor for the $La_{0.8}Ca_{0.2}FeO_3$, $La_{0.8}Gd_{0.2}FeO_3$ and $LaFe_{1-x}Mg_xO_3$ (x = 0.05 – 0.2).

4) Thermogravimetric analysis

The oxygen stoichiometry for the system $LaFe_{1-x}Mg_xO_3$ (x = 0.05 – 0.2) was analysed by thermogravimetric analysis with a heating rate of 10 K/min in the reactive gas of H_2 (Figure 10). The TG curve show that the weight loss started slowly at about 530 K followed by a faster loss which was completed at about 1450 K. The products which we obtained were analyzed by XRD. A weight loss of 8.44 – 9.29 % was found, which is corresponding to the oxygen stoichiometry $LaFe_{0.8}Mg_{0.2}O_{2.947}$, $LaFe_{0.85}Mg_{0.15}O_{2.978}$, $LaFe_{0.9}Mg_{0.1}O_{2.971}$ and $LaFe_{0.95}Mg_{0.05}O_{2.951}$.

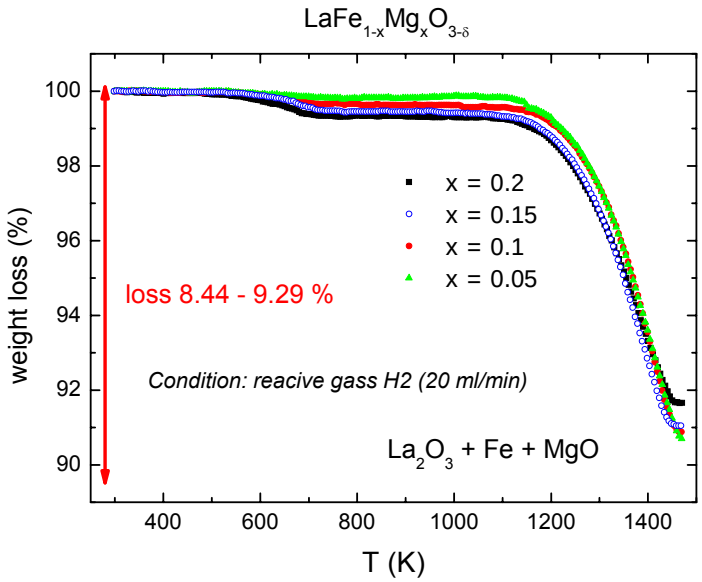


Figure 10: TG curve of the $LaFe_{1-x}Mg_xO_3$ (x = 0.05 – 0.2) measured in the reactive gas of H_2 with a heating rate of 10 K/min.

5) $Gd_{1-x}Sr_xCoO_3$ system

The samples of the system $Gd_{1-x}Sr_xCoO_3$ (x = 0.2, 0.3, 0.5) were prepared by a conventional solid-state chemistry with using Gd_2O_3, $SrCO_3$ and CoO as the starting materials. These powders were mixed in the right molar ratios in an agate mortar and calcinated at 1073 K in air and further at 1473 K for several hours at the same conditions. After calcination, the samples were pressed in form of pellets and sintered at the same temperature for 12 hours in air (heating/cooling rate 5 K/min).

The temperature dependence of the electrical resistivity of the samples with x = 0.2, 0.3 is showing semiconducting behaviour (Figure 11a) with the activation barrier at about 650 – 700 K, while $Gd_{0.5}Sr_{0.5}CoO_3$ is more metallic than semiconducting with an approximately ten times smaller value of electrical resistivity at 340 K than the compounds with x = 0.2, 0.3.

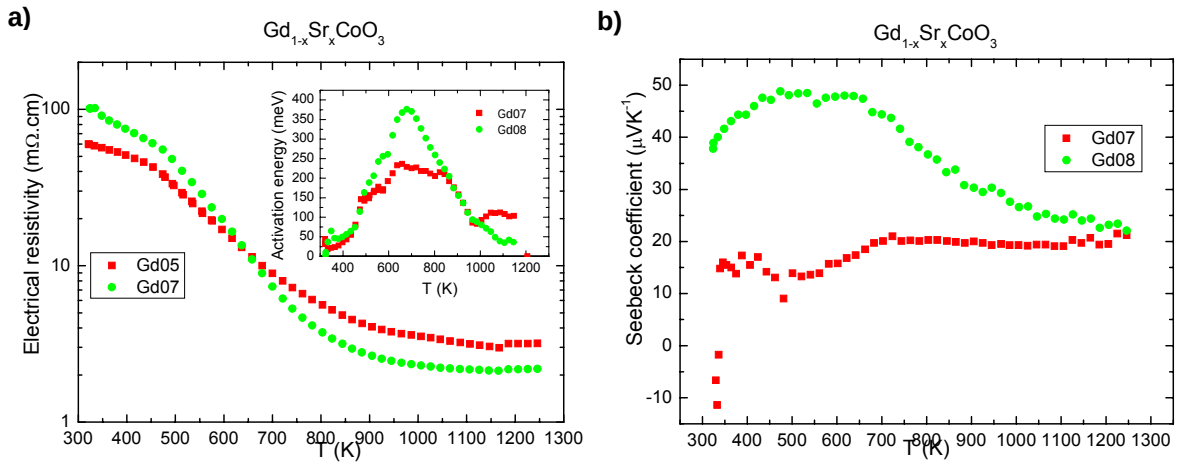


Figure 11: Temperature dependence of the electrical resistivity with the inset of activation energy (a) and temperature dependence of the Seebeck coefficient (b) for the $Gd_{1-x}Sr_xCoO_3$ (x=0.2, 0.3 and 0.5).

The Seebeck coefficient has a positive character in the whole temperature range indicating p-type charge carriers. The Seebeck coefficient of the $Gd_{0.5}Sr_{0.5}CoO_3$ (Figure 11b) has the lowest value, typically for metallic compounds. The Seebeck coefficient of the sample with x = 0.3 has the constant value at above 700 K. Temperature dependence of the power factor is plotted on Figure 12 with the largest value of $4x10^{-5}$ $WK^{-2}m^{-1}$ for the sample $Gd_{0.8}Sr_{0.2}CoO_3$.

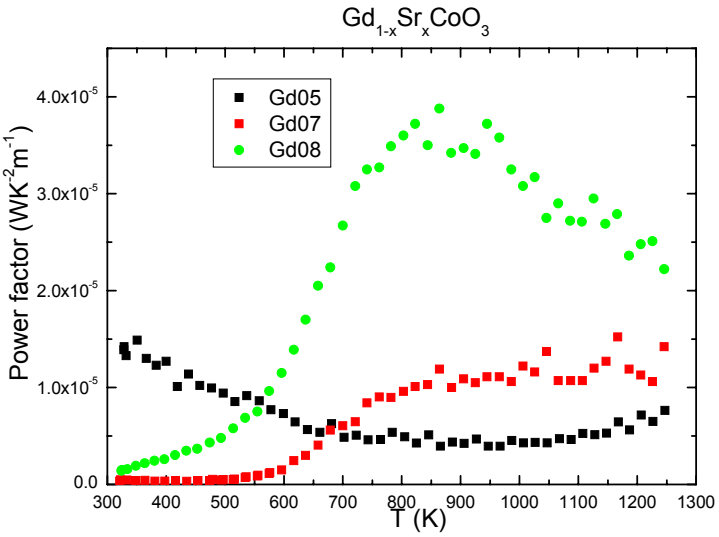


Figure 12: Temperature dependence of the power factor for the $Gd_{1-x}Sr_xCoO_3$ (x=0.2, 0.3 and 0.5).

Nationale Zusammenarbeit

- Andreas Bitschi, Klaus Fröhlich, Electric Power Transmission and High Voltage Technology Laboratory, ETHZ: Modeling and simulation of the coupled thermal and electric systems.

Internationale Zusammenarbeit

- F. Spirovski, Anorganische Chemie I, Universität Siegen, Germany – Electric properties of tri-nickel tin ditelluride, $Ni_{3-x}SnTe_2$
- Dr. J. Hejtmanek, Institute of physics ASCR, Prague, Czech Republic

Bewertung 2007 und Ausblick 2008

The *n*- and *p*-type thermoelements were connected in series by highly conducting silver with CuO on the alumina plate. Thermoelectric modules with different legs-length were measured in order to find the best generator's performance. The temperature gradient between the hot and the cold side decreased with decreasing thermoelement length. The maximum power output was obtained for 2 mm lenght legs The conversion efficiency was found to be the best for Δ T = 500 °C. New materials which can be perspective as new potential *p*-type thermoelectric oxide materials were investigated.

For the future work involves the crystal structure determination of the new materials by the Rietveld method, continuing the synthesis with changing the ratio of dopand elements, synthesis in oxidizing atmosphere, studies at the low temperature and in the magnetic field. The samples will be analyzed by XPS to determine the oxidation state of cations.

Referenzen

[1] R. Robert, M.H. Aguirre, P. Hug, A. Reller, A. Weidenkaff, Acta Materialia 55 (2007) 4965–4972.

[2] L. Bocher, R. Robert, M.H. Aguirre, S. Malo, S. Hébert, A. Maignan, A. Weidenkaff, Solid State Sciences, in press.

List of conference contributions and scientific publications in the 2007 funding period

- "Properties of four-leg thermoelectric oxide modules (TOM) for electric power generation" P. Tomes, M. Trottmann, A. Bitschi, E. Hack,S. Toggweiler, L. Bocher, R. Robert, M. H. Aguirre, A. Weidenkaff, Empa Phd students day, Empa (Dübendorf, Switzerland) Nov 2007.
- "Transport properties of ferrates for high temperature thermoelectric applications", P. Tomes, M. Trottmann, L. Bocher, R. Robert, D. Logvinovich, M. H. Aguirre, A. Weidenkaff, 6th Empa-PSI Phd students day, PSI (Villigen, Switzerland)Nov 2007.