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Umwelt, Verkehr, Energie und Kommunikation UVEK

Bundesamt für Energie BFE

GEO-THERMOPOWER

GEO-TEP MATERIALS

Jahresbericht 2006

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ZUSAMMENFASSUNG

The morphological, microstructural and thermoelectric properties of two different perovskite-type manganate systems were investigated. The predominance of the transition metal (either cobalt or manganese) influences strongly the transport and thermal properties of $LaMn_{1-x}Co_xO_{3\pm\delta}$ (with x=0.05; 0.10; 0.90; 0.95). A *n*-type semiconductor material: $CaMn_{1-x}Nb_xO_{3\pm\delta}$ (with x=0.02; 0.05; 0.08 and 0.10) reveals promising thermoelectric properties in a large temperature range. A power factor: $PF = S^2/\rho$ of 2, 47.10^{-4} $W.m^{-1}.K^{-2}$ is obtained at 870 K for $CaMn_{0.92}Nb_{0.08}O_{3\pm\delta}$. Various particle morphologies and sizes were obtained based on soft chemistry synthesis methods using different thermal processes: bulk decomposition method or Ultrasonic Spray Combustion (USC).

Projektziele

Thermoelectricity is a direct energy-conversion technology transforming heat into electricity. It reveals environmental and economical advantages such as: (i) e.g. geothermal heat conversion, (ii) electric power sources without producing toxic exhausts and moving parts, (iii) and long operating lifetime. Since established thermoelectric materials (e.g. BiTe, PbTe) are toxic, scarce and expensive material research is recently dedicated to the development of perovskite-type cobaltate, manganate or titanate oxides exhibiting promising thermoelectric activities. Oxide-type materials are interesting due to their low production cost as well as their chemical and thermal stability for a large range of temperature in air.

A compromise between high power factor ($S^2\sigma$) and low thermal conduction (κ) is required to optimise ZT. Studies on phonon boundary scattering for submicron-sized polycrystalline grains predict lower lattice thermal conductivities without altering the electron mobility [5]. This challenge can be achieved by developing new synthesis processes which improve the thermal properties of the potential oxide materials. Polycrystalline perovskite particles are successfully synthesised by a complexation soft chemistry method leading to smaller particles by decreasing significantly synthesis time and temperature compared to the conventional ceramic route. Micro-TOMs (Thermoelectric Oxide Modules) allow electricity generation from small temperature gradients. The geothermal processes exploit temperatures in the range of 300 K – 600 K therefore heat conduction reduction by phonon scattering and high exchange surface areas can be used to design micro-TOMs converters.

Promising *p*-type oxides are identified but *n*-type semiconductors are an indispensable part of thermoelectric oxide modules. Up to now none of the *n*-type oxide materials have thermoelectric performance comparable to the state of art layered cobalt oxides as Na_xCoO_2 [1] or $Ca_3Co_4O_9$.[2]. Investigations are still required to find a potential *n*-type oxide thermoelectric material. The undoped $CaMnO_3$ perovskite-type compound shows at 300 K a large negative thermopower ($S = -350\mu V.K^{-1}$) with a high resistivity ($\rho = 2\ \Omega.cm$). Lower resistivity results from low-level doping. $CaMnO_3$ can be substituted by two different efficient ways to adjust the carrier density and therefore obtain a higher ZT value. One possibility is the substitution on the Ca site as reported by Maignan *et al.* [3], another way is doping Mn-site with cations having a valency higher than 4^+. Thus the $CaMn_{1-x}Nb_xO_3$ compounds may be a potential thermoelectric system. The Nb substitution in the $CaMnO_3$ system significantly decreases the resistivity in the low temperature region (T < 400 K) as reported by Raveau *et al.*[4]. Our interest is more focused in the high temperature thermoelectric performance (T > 300K) thus the $CaMn_{1-x}Nb_xO_3$ system with low substitution level was studied above room temperature as potential thermoelectric material.

Durchgeführte Arbeiten und erreichte Ergebnisse

1. Soft chemistry perovskite particles: morphology and microstructure.

Polycrystalline perovskite-type phases were synthesised by *chimie douce* synthesis method with emphasis on low synthesis temperature (873 K < T < 1073 K) [6]. Either stepwise calcinations (bulk method) or a continuous combustion process (Ultrasonic Spray Combustion - USC) were used to decompose the corresponding citrate precursor prepared by soft chemistry synthesis method. Both synthesis methods lead to pure perovskite phases. A flow chart indicates synthesis procedures and characterization methods in Figure 1.

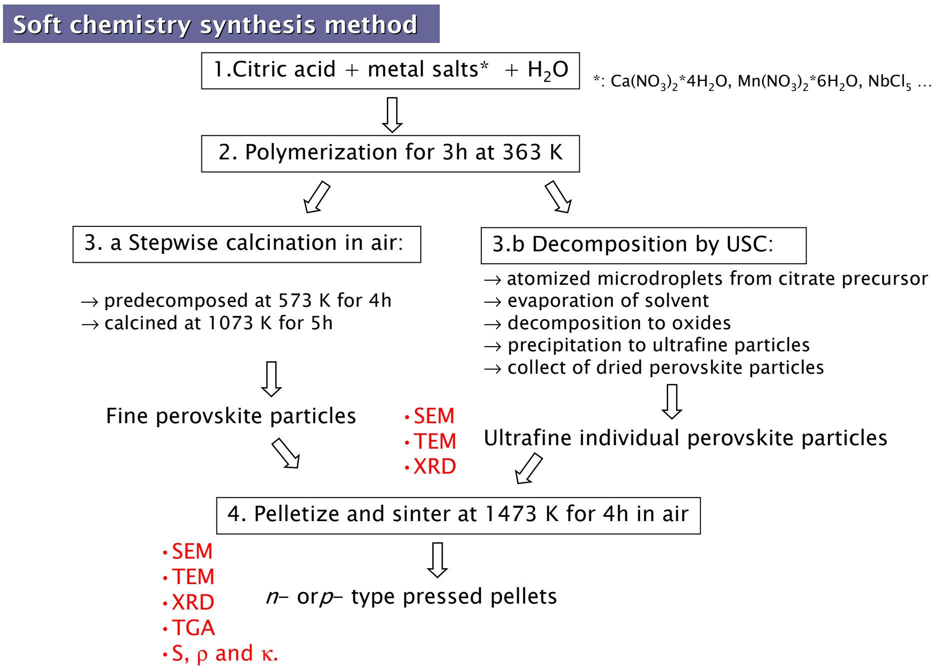


Figure 1: Flow chart indicating the both synthesis procedures and characterization methods (in red). The morphology of the perovskite powders and the pellet cross section was investigated with a Scanning Electron Microscope (SEM) LEO JSM-6300F. The perovskite particles were studied concerning their microstructures with a Transmission Electron Microscope (TEM) Philips CM 30. Samples were prepared by dispersing ground powder in ethanol and were therefore deposited on a holey carbon film. Transport properties (thermopower: *S* and resistivity: ρ) were measured simultaneously in the range of 313 K-1273 K in air with 20 K steps using an Ozawa RZ2001i unit. Thermal conductivity (κ) measurements were performed on disc-shaped pellets under argon for 300 K < T < 1000K every 50 K.

- The citrate precursor is thermally treated by successive calcination steps leading to pure perovskite phases. Fine agglomerated and partly-sintered spherical particles are achieved by this bulk decomposition method (see Figure 2a.). Submicrometer grains are obtained at higher temperatures due to the growth of the agglomerated particles by sintering effect.
- Microdroplets of the same citrate precursor can be heat treated in an aerosol process using Ultrasonic Spray Combustion method (USC). The precursor solution is nebulized with a piezoelectric transducer at a frequency of 1.67MHz in a flow of air. The droplets of citrate precursor are transported into a high temperature reactor to obtain perovskite particles. The fine oxide particles are collected in a glass fibber filter heated at 423 K.

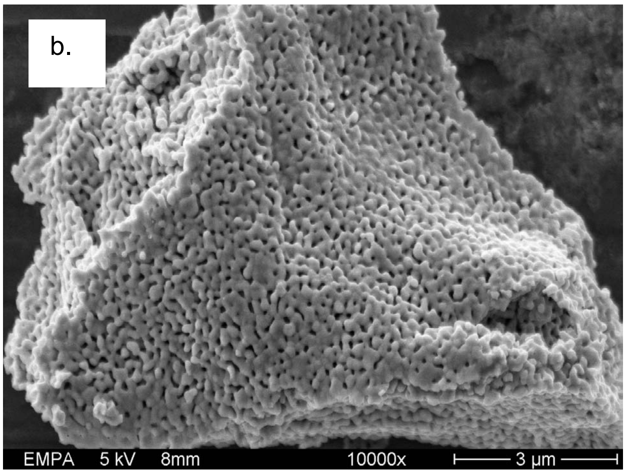


Figure 2 a.: SEM micrograph picture of perovskite particles decomposed by the bulk method (at 1073 K for 4h).

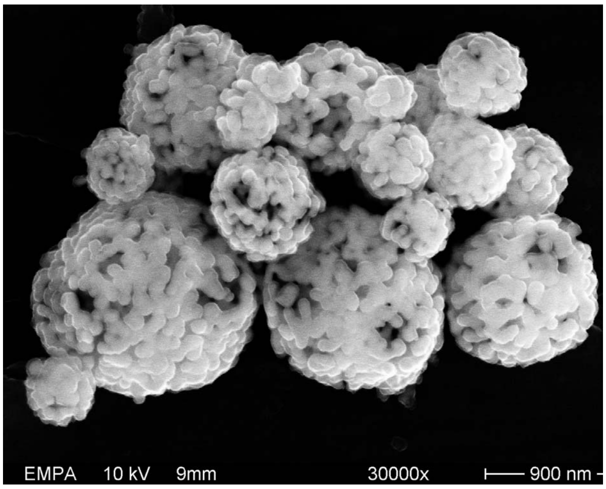
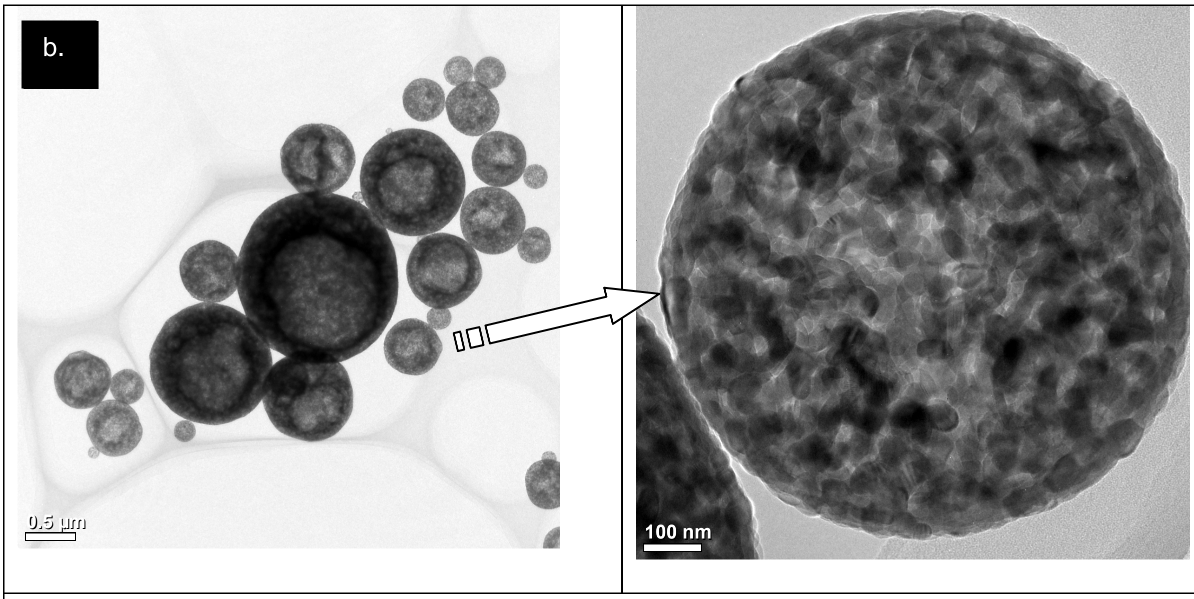


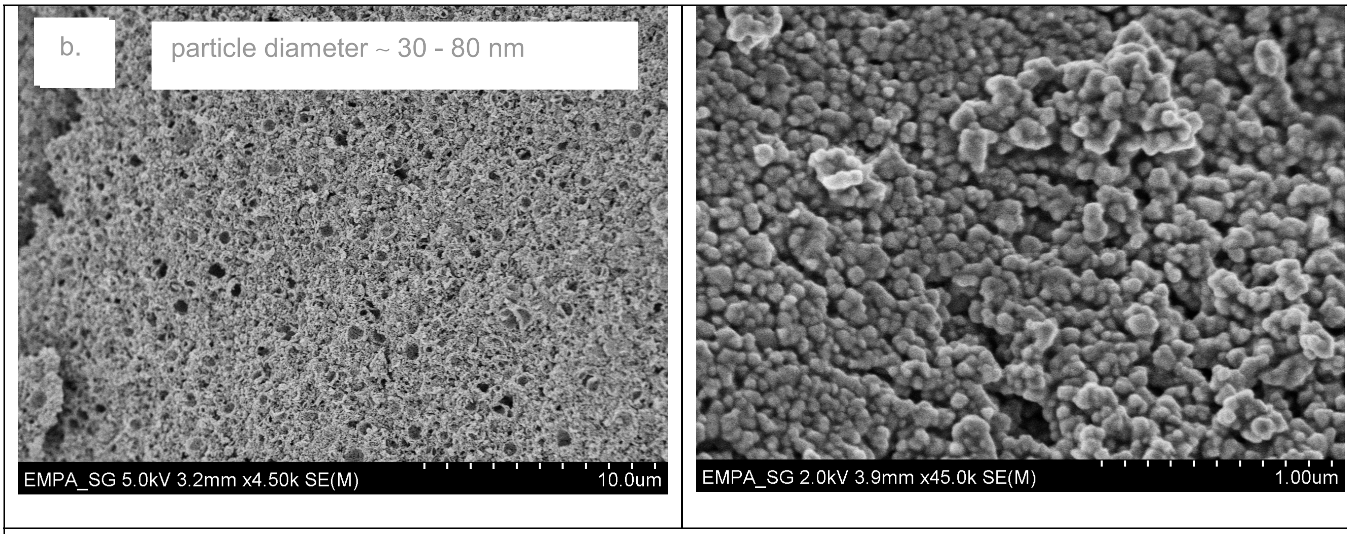
Figure 2 b.: SEM micrograph pictures of CaMn$_{0.95}$Nb$_{0.05}$O$_{3\pm\delta}$ particles produced by USC: hollow spheres forming by ultrafine perovskite particles.

The SEM image, see Figure 2.b, reveals hollow spheres produced by USC which are formed by ultrafine and homogeneous perovskite particles. These oxide spheres are structured by ultrafine crystalline particles of approximately 20 nm diameter (Figures 3 a. and 3 b.).



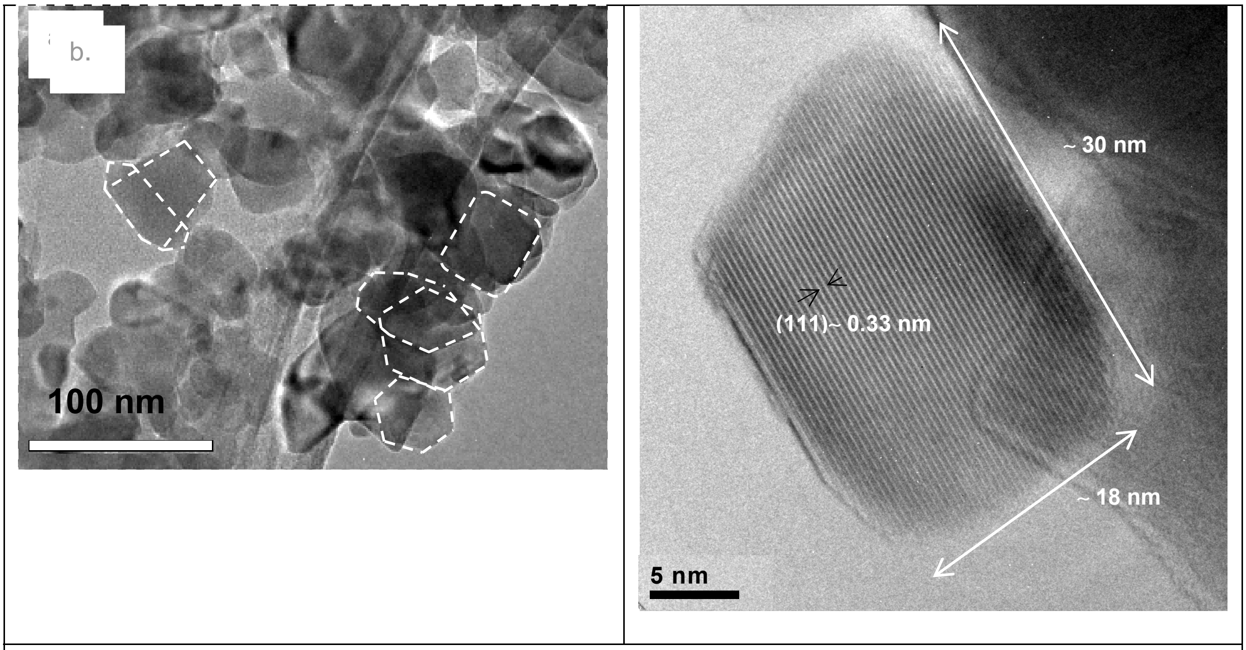
Figures 3 a. and 3 b.: TEM images of the perovskite spheres (100nm to 3 μm diameter) formed by ultrafine particles (particle diameter ~ 20nm) - $T_{\text{furnace}} = 1223$ K.

The sphere size distribution can fluctuate depending on the USC experimental conditions. Different technical parameters (furnace temperature, gas flow, solution concentration and citric acid/cations ratio) were adjusted concerning the influence and the correlation on the particle morphology as well as the production rate. The production of large quantities of pure oxide powder is possible by the continuous USC process (~ 200 mg/h). The USC process avoids the particle agglomeration reducing the particle diameter by a factor 3 to 10 (depending on the different experimental conditions: furnace temperature, gas flow, solution concentration…) compared to the bulk thermal decomposition.



Figures 4 a. and 4 b.: SEM micrograph pictures of sintered pellet at 1473 K for 6h (produced from USC particles)

The perovskite particles produced by USC were pressed and sintered at 1473 K for 6h. Sintering effect on perovskite pellets were studied by means of SEM and TEM investigations (Figures 4 a. and 4 b.). The cross sectional view of the pellet (Figure 4 a.) reveals sintered and compact spherical grains with a homogeneous size distribution. A microstructure detail of the sintered pellet (Figure 4 b.) shows ultrafine grains of 30 to 80 nm diameter. The microstructure of the sintered pellet exhibits nanometer-size grains as shown in Figure 5 a. The High Resolution TEM image shows a well-defined highly crystalline material indexed as orthorhombic perovskite-type structure (Figure 5 b.). No amorphous domains, crystalline impurities or secondary phases are found. The sintering of the USC particles does nearly not affect the particle growth leading to crystallite size below 100nm.

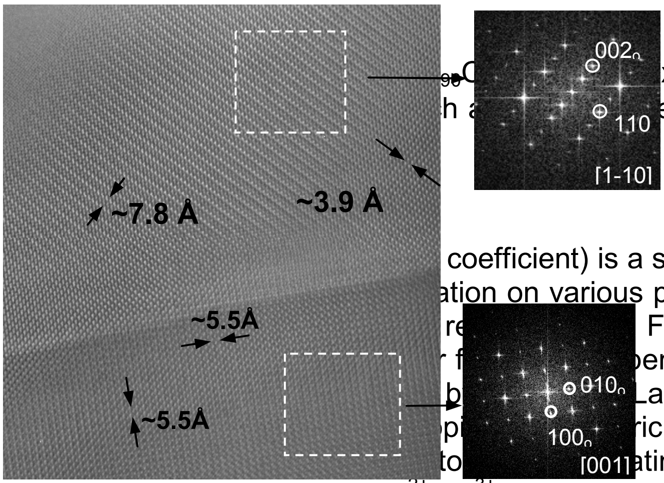


Figures 5 a. and 5 b.: TEM and HRTEM images of sintered pellet ($CaMn_{0.95}Nb_{0.05}O_3$) at 1473 K produced from USC perovskite particles: grain size from 20 to 50nm. HRTEM image indexed as orthorhombic structure (*Pnma*).

Perovskite particles synthesized by bulk thermal decomposition reveal typical submicrometric grains due to the high sintering temperature [6]. While the particles produced by the USC method lead to nanometric size even after sintering processes [7]. These ultrafine USC perovskite particles appear more suitable to form pellets without major increase of the particle size and thus more appropriate as thermoelectric materials.

2. $LaMn_{1-x}Co_xO_{3\pm\delta}$ system [8]:

Submicrocrystalline particles of $LaMn_{1-x}Co_xO_{3\pm\delta}$ (with x = 0.05, 0.10, 0.90, 0.92, 0.95 and 0.98) were synthesised by bulk thermal decomposition of the citrate precursor. The Co-rich compounds crystallize in the rhombohedral structure (R3c) while the Mn-rich compounds present microdomains of orthorhombic structure (Pbnm). High resolution micrographs and respective FFT for orthorhombic structure ($a_p\sqrt{2}$ *x* $a_p\sqrt{2}$ x $2a_p$ with a_p ~ 3.9Å normal cubic perovskite parameter) are presented in Figure 6. Two microdomains are observed with the zone axis $(3)_p\leftrightarrow(3)_o$ and $(4)_p\leftrightarrow[1\text{-}10]_o$ (subscripts p and o mean perovskite basic cubic cell and orthorhombic one, respectively). The domains present a long range of ordering without any defect or dislocation. The TEM studies confirm a highly crystalline and chemically homogeneous appearance for all compounds. No amorphous domains, crystalline impurities or secondary phases are found.



90C xed as orthorhombic structure (Pbnm: a = h ed to cubic perovskite parameters ~ $a_p\sqrt{2}$x

coefficient) is a sensitive probe of the entropy per carrier in ation on various physical phenomena. The temperature de- re Figure 7 for all the compositions. The sign f pend mainly on the nature of the charge car- b $LaMnO_3$ matrix induces a Mn^{3+}/Mn^{4+} mixed p rich compounds (x = 0.05 and 0.10) exhibit to ting predominant hole-like carriers. N-type doping is generated by the Co^{2+}/Co^{3+} mixed valency due to the substitution of Co by Mn in the $LaCoO_3$ system. With 5 % of Mn in the $LaCoO_3$ system, a negative Seebeck value is obtained at 340 K which indicates predominant electron-like carriers ($S_{340K} = -82.1\mu VK^{-1}$). The evolution of S(T) shows a sign change with temperature. This change of *n*-type to *p*-type conduction for slightly Mn-doped compounds reveals that the carrier type is modified at high temperature. This can be explained by:

i. a disproportion of the Co ions
ii. a change of carrier concentration and mobility
iii. a spin state changes of Co [7].

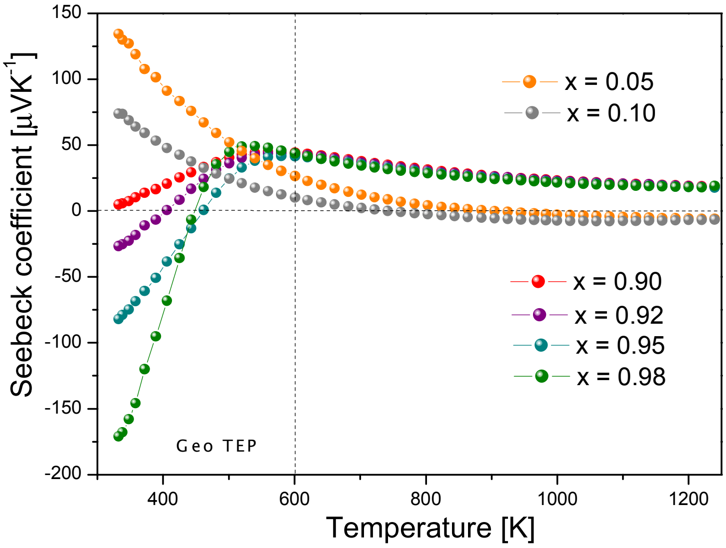


Figure 7: Temperature dependence of the Seebeck coefficient for the $LaMn_{1-x}Co_xO_{3\pm\delta}$ (x=0.05, 0.10, 0.90; 0.92; 0.95; 0.98).

The electrical resistivity of the Co-rich samples (x = 0.90 and 0.95) decreases sharply with the temperature up to 700 K, which corresponds to a semiconducting-like behavior ($d\rho/dT<0$) (Figure 8 a.). Above 800 K the Co-rich compounds show highly conductive behavior keeping the electrical resistivity constant up to 1240 K (ρ = 1.21 mΩ cm for x = 0.95 and ρ = 1.35 mΩ cm for x = 0.90). The thermopower sign change and a low electrical resistivity above 500-600 K illustrate the presence of activated hole-like carriers. The high temperature behaviour of the Co-rich compounds could be explained as the disproportion of Co^{3+} into Co^{2+} and Co^{4+}. Thus a maximum power factor (PF = $7{,}1.10^{-5}$ $W.m^{-1}.K^{-2}$ for x = 0.95) is obtained at 700 K.

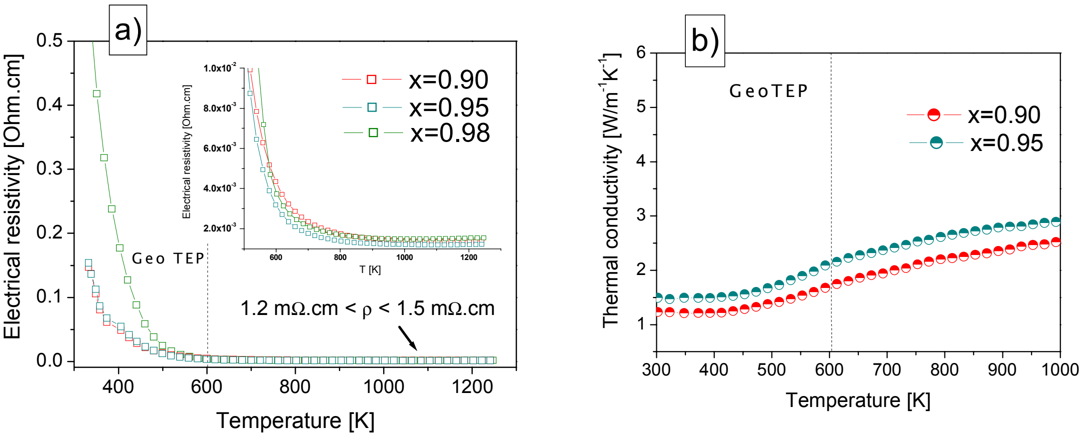


Figure 8 a. and 8 b.: Temperature dependence of the electrical resistivity for the $LaMn_{1-x}Co_xO_{3\pm\delta}$.(x=0.90; 0.92; 0.98) (a.). (Inset: electrical resistivity as function of T for in the range of 500 K <T< 1240K) and the total thermal conductivity for $LaMn_{1-x}Co_xO_{3\pm\delta}$ (x = 0.90 and 0.95) (b.).

The thermal transport properties of these compounds were investigated in the large temperature range of 300 K < T < 1000K (Figure 8 b.). Below 500 K the cobaltate-rich compounds display low thermal conductivity values (κ < 1.8 $Wm^{-1}K^{-1}$). The Co-rich samples exhibit a large increase of the heat conductivity with increasing temperature. The total thermal conductivity of a solid consists of the phonon contribution κ_{ph} and the electronic contribution κ_e.

The electronic component is related to the electrical conductivity σ in the Wiedemann-Franz's law: $\kappa_e = L_0 \, \sigma \, T$, where L_0 is the Lorentz number and T the absolute temperature [10]. The phonon conductivity is overwhelmed for the cobaltate compounds below 500 K. The lattice contribution influences mainly the heat conduction with κ_e < 0.15% of the total thermal conductivity.

3. $CaMn_{1-x}Nb_xO_{3\pm\delta}$ system [7]:

Ultrafine particles of $CaMn_{1-x}Nb_xO_{3\pm\delta}$ (with x = 0.02; 0.05; 0.08 and 0.10) were successfully synthesised by USC. The whole manganates series exhibit orthorhombic structure (space group: *Pnma*). All compounds present negative thermopower values for the whole temperature range (340 K < T < 1240K) indicating electron as predominant charge carriers (Figure 9). The substitution of Nb^{5+} in the $CaMnO_3$ system generates certainly Mn^{3+} ions and therefore an increase of the electron concentration in the perovskite-type manganates. The absolute Seebeck values decreases as the Mn^{3+} content increases but remains significantly large (e.g. $S_{1098\ K}$ = -129µV.K^{-1} for x = 0.10 and $S_{1063\ K}$ = -182µV.K^{-1} for x = 0.02). With increasing temperature the absolute thermopower value rises e.g. from $S_{373\ K}$ = -123 µV.K^{-1} to S_{1044K} = -173 µV.K^{-1} for x = 0.05.

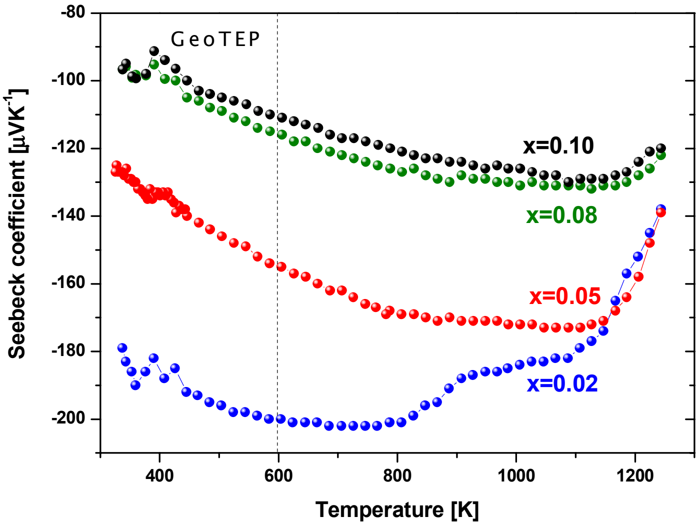


Figure 9: The temperature dependence of thermopower of $CaMn_{1-x}Nb_xO_{3\pm\delta}$ (with x=0.02; 0.05; 0.08 and 0.10).

The ρ values are consistent to the reported data at low temperature region [4] and gradually decrease with increasing the Nb content (e.g. ρ = 19 mΩ.cm for x= 0.02 to ρ = 7 mΩ.cm for x= 0.08 at 400K), see Figure 10. The doped compound with 8% Nb presents metallic-like transport behaviour. Low content of Jahn Teller Mn^{3+} ions favors a metallic behaviour in the $CaMn_{1-x}Nb_xO_{3\pm\delta}$ system. A decrease of the absolute Seebeck coefficient value is induced. The introduction of electrons in the Mn^{4+} matrix has beneficial effects on resistivity which can reach ρ < 10 mΩ.cm for x = 0.08 in the whole temperature range. For similar holes concentrations in $LaMnO_3$ resistivity values are twice time higher [8]. The electron doped manganate appears as better candidates than their hole-doped counterparts. The resistivity and thermopower of the $CaMn_{0.98}Nb_{0.02}O_3$ shows anomalies at 800K and 1000K. This phenomenon occurs also at 800K for a similar composition $CaMn_{0.98}Ru_{0.02}O_3$ [11]. The oxygen content variation at high temperature could cause these changes observed on the thermopower and resistivity evolution. Studies on the oxygen stoichiometry are in progress.

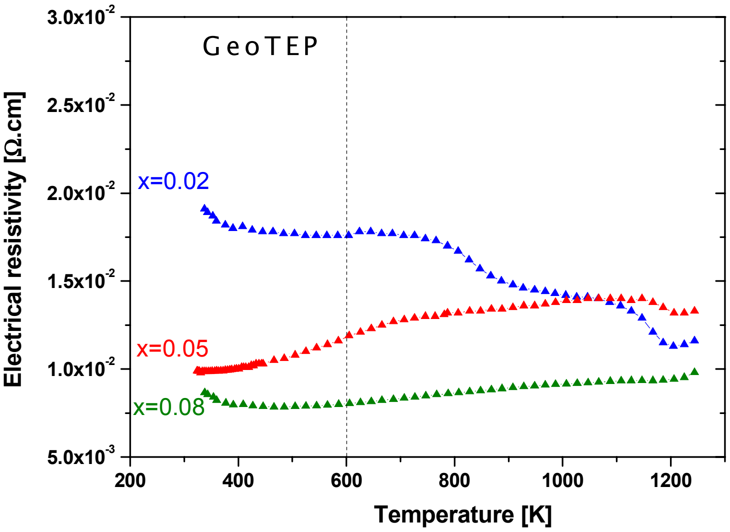


Figure 10: The temperature dependence of electrical resistivity of $CaMn_{1-x}Nb_xO_{3\pm\delta}$ (with x=0.02; 0.05 and 0.08).

Large power factor values ($PF = S^2/\rho$) are achieved for a broad temperature range. 2% Nb in the $CaMnO_3$ system leads to a PF > $2{,}2.10^{-4}$ $W.m^{-1}.K^{-2}$ for 520 K < T < 1150 K with a maximum of $2{,}4710^{-4}$ $W.m^{-1}.K^{-2}$ at 870 K. A similar behaviour is observed for the other compounds with smaller power factor values. The small doping level is responsible for a metallic behaviour together with a relatively large Seebeck coefficient which makes this material interesting as an *n*-type thermoelement. Thermal conductivity measurements were performed by the laser flash method. The compound with a higher power factor ($CaMn_{0.92}Nb_{0.08}O_3$) exhibits a thermal conductivity below 3.5 $W.m^{-1}.K^{-1}$ for 300 K < T < 1000K. The Z value of $CaMn_{0.92}Nb_{0.08}O_3$ egal to $0{,}85.10^{-4}$ K^{-1} at 870 K which is larger than most of the others *n*-type oxide materials i. e. $0{,}17.10^{-4}$ K^{-1} for $Nd_{2-x}Ce_xCuO_4$ [11], $0{,}40.10^{-4}$ K^{-1} for In_2O_3-based mixed oxides [13] and $0{,}70.10^{-4}$ K^{-1} for $Ca_{0.9}Bi_{0.1}MnO_3$ [14].

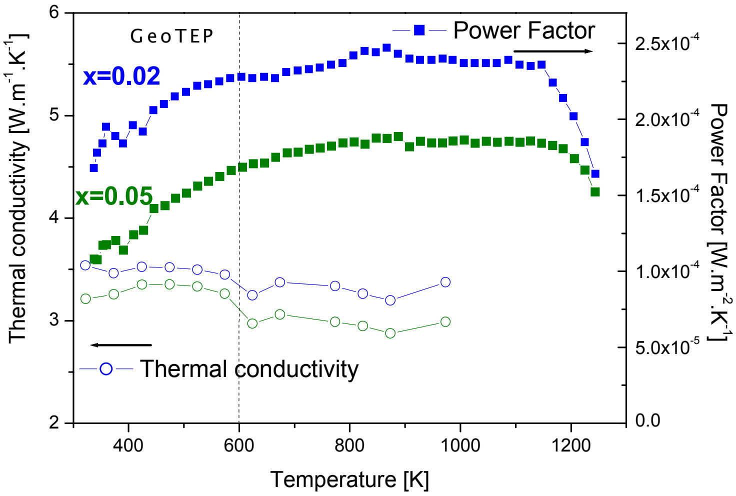


Figure 11: The temperature dependence of power factor and thermal conductivity of $CaMn_{1-x}Nb_xO_{3\pm\delta}$ (with x=0.02 and 0.05).

Nationale Zusammenarbeit

- Klaus Fröhlich, Electric Power Transmission and High Voltage Technology Laboratory, ETHZ: System design packaging of the thermoelectric module. Modeling and simulation of the coupled thermal and electric systems.
- T. Kaspar and Prof R. Nesper, ETH Zürich, Laboratory of Inorganic Chemistry – Si/B/N/C ceramics
- Dr. T. Quan, ETH Zürich, Laboratory for Nanometallurgy - Ni superalloy (Ni-Cr-Co base)- zirconia composites

Internationale Zusammenarbeit

- Dr. A. Maignan, CRISMAT, UMR 6508 CNRS/ENSICAEN – France - Thermal properties on complex oxide structures
- Dr. J. Hejtmanek, Institute of Physics ASCR – Prague. Czech Republic - Thermal properties on complex oxide structures

Bewertung 2006 und Ausblick 2007

The laboratory of Solid State Chemistry acquire in 2006 two new set-ups for the measurements of thermoelectric properties in the temperature range of 300 K-1273 K (Ozawa RZ2001i unit to measure thermopower and resistivity, Netzsch LFA 457 Micro Flash for the thermal conductivity determination). These measurement units are unique in Switzerland owing us to well characterize functional thermoelectric materials.

The USC method based on the soft chemistry techniques was successfully applied as a continuous process to obtain pure perovskite-phases. Preliminary studies on particle morphology and microstructure reveal highly crystalline nanometer-size grains. Further investigations are in progress to correlate morphology and thermoelectric properties of the nanometric and submicrometric perovskite crystallites.

Perovskite-type manganate phases were investigated as potential *n*-type thermoelectric oxide materials. The $CaMn_{1-x}Nb_xO_{3\pm\delta}$ system presents a metallic-like behaviour (dependent on the substitution level) with large negative Seebeck coefficients for the whole high temperature range. High power factor were achieved making this perovskite-type oxide interesting as *n*-type thermoelement.

More detailed studies on the thermal conductivity reduction are still required for a better understanding of the phonon thermal transport. The heat capacity (Cp) is a crucial parameter to determine κ. Further investigations on Cp influence will be studied with a new DSC set up dedicated to the Cp measurements up to high temperatures. Micro-TOMs dedicated to low temperature gradients will be built up at Empa based on *p*- and *n*-type oxide thermoelectric materials. The thermoelements will be synthesised based on the USC method.

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[7] L. Bocher, M. H. Aguirre, M. Trottmann, Robert, R. and A. Weidenkaff, in preparation

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List of conference contributions and scientific publications in the 2006 funding period:

- “Development of perovskite-type materials for thermoelectric technologies” Bocher, L., (oral), 4rd Empa – PSI PhD students day, PSI (Villigen, Switzerland), 24. October 2006.

- Bocher, L., Robert, R., Logvinovich, D., Shkabko, A., Burchhardt-Herold, S., Aguirre, M. H., Trottmann, M., and Weidenkaff, “Cationic and Anionic Substitution in Functional Perovskite-type Phases” (poster). SCS meeting, University of Zürich, 13. October 2006

- “Thermoelectric perovskite-type oxides as functional materials for high temperature solar energy conversion”, Robert, R., Aguirre, M. H., Bocher, L., Trottmann, M. and Weidenkaff, A. (oral), 25th International Conference on Thermoelectrics, (Vienna - Austria), 6-10 August 2006.

- “Nanocrystalline domains influence on thermoelectric materials”, Aguirre, M. H., Robert, R., Bocher, L., Trottmann, M. and Weidenkaff, A. (oral), 25th International Conference on Thermoelectrics, (Vienna - Austria), 6-10 August 2006.

- “Thermal conduction in thermoelectric perovskite-type oxides” Bocher, L., (oral), 3rd Empa – PSI PhD students day, Empa (Dübendorf, Switzerland), 14 June 2006.

- “Development of Thermoelectric Oxides for Renewable Energy Conversion Technologies” Weidenkaff, A., Robert, R., Aguirre, M. H., Bocher, L., Lippert, T. and Canulescu, S. (oral), E-MRS 2006 Spring Meeting (E-MRS - IUMRS - ICEM 06), (Nice, France), 29 May 2nd June 2006.

- Bocher, L., Robert, R., Aguirre, M. H., Trottmann, M., Hug, P., Heeb, N., Weidenkaff, A. “Nano-and Micro-Porous Materials Synthesis and Analysis for Catalytic and Thermoelectric Applications" (poster), FOKO C, Empa (Dübendorf, Switzerland), 12 May 2006.

- "Thermoelectric perovskite-type oxides for geothermal and solar energy conversion" Bocher, L., Robert, R., Aguirre, M. H., Schlapbach, L. and Weidenkaff, A., (oral), 4th European Conference on Thermoelectrics, Cardiff University (UK), 9-11 April 2006.
- "Geo-thermoelectric converters" Bocher, L. (oral), Solid State Chemistry Seminar, Empa (Dübendorf, Switzerland), 7 February 2006.
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