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SOLAR-TEP

MATERIALENTWICKLUNG FÜR SOLAR-THERMISCHE STROMERZEUGER

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Autor und Koautoren	Rosa Robert and Anke Weidenkaff
beauftragte Institution	Empa
Adresse	Ueberlandstr.129
Telefon, E-mail, Internetadresse	+41 44 823 4131
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ZUSAMMENFASSUNG

The effect of Ti and Ni substitution into the $LaCoO_{3-\delta}$ system and the effect of Ln substitution of the $LnCo_{0.95}Ni_{0.05}O_{3\pm\square}$ was studied by means of electrical conductivity and Seebeck coefficient measurements in a broad temperature range to enhance the thermoelectric properties of the new thermoelectrics. A series of single phase products with a nominal composition of $LaCo_{1-x}Ni_xO_{3-\delta}$, $(0.02 \leq x \leq 0.20)$, $LaCo_{1-x}Ti_xO_{3\pm\delta}$, (0.01, 0.10, and 0.20), and $LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$ (Ln = La, Pr, Nd, Sm, Gd) were prepared by a soft-chemistry process. Pure phases were obtained at relatively low temperature, i.e. at T = 873 K. The power factor, $PF = S^{2}*\square$, for the Ni substituted samples is $PF = 1.42*10^{-4}$ $W/m^{2}*K$ for x = 0.10 at T = 540 K. Ti substitution leads to a higher power factor compared to that of Ni substitution at T = 1240 K.
The variation of the lanthanide ionic radii influences the crystal structure and thus the transport properties. While the $LaCo_{0.95}Ni_{0.05}O_{3-\square}$ crystallized in rhombohedral crystal structure, the parent compounds with smaller rare-earth cations crystallized in orthorhombic crystal structure. The decreasing lanthanide ionic radii ($Pr^{3+} > Nd^{3+} > Sm^{3+} > Gd^{3+} > Dy^{3+}$) lead to an enhanced lattice distortion. These structural changes affect the thermoelectric properties of the $LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$ system, i.e. the temperature of the undesirable semiconductor to metal transition shift with decreasing rare-earth ionic radii to higher temperature.

Projektziele

Solar energy can be directly converted into electrical energy by thermoelectric power generators. Compared to photovoltaic technology, which is mostly limited to the UV-part of the solar radiation, thermoelectric devices can harvest energy from the whole solar radiation spectrum. The advantage of the **Empa-thermoelectric oxide modules** (**TOM**) is the possibility to enlarge the operating range of temperature and thus the efficiency due to the high stability of oxides at high temperatures in air. Furthermore, thermoelectric oxide devices can be realised on the basis of low cost materials with low toxicity. The scope of thermoelectricity applications depends on the thermoelectric output power which is directly increased with the temperature difference over which the device is operating, and the thermoelectric activity of the material which depends on the so called figure of merit, $Z = S^2/\rho\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity and κ is the thermal conductivity. Operation at a temperature of T = 1200K, cold junction at T = 300K, enhances as well the theoretical heat into electricity conversion efficiency, η, to around 15% for a Z value of 0.001 K^{-1} calculated by the following equation, Eq. (1) [1]: $\eta = \frac{T_H - T_C}{T_H} * \left(\frac{(\sqrt{1+ZT}) - 1}{(\sqrt{1+ZT}) \frac{T_H}{T_C}} \right)$, where T_H and T_C are the temperature at the hot and cold junction respectively, T is the average of the T_H and T_C, Z is the dimensionless figure of merit of the thermoelectric couple.

The toxic and unstable state-of the-art thermoelectric oxide materials display a figure of merit value, ZT, around the unity. New oxides e.g. Na_xCoO_3 single crystal shows a Z = 0.001 K^{-1} at T = 800K (ZT = 0.8).

Thus, it can be concluded that essential the **improvement of the output power** requires the development of novel functional materials with enhanced figures of merit, Z, and high temperature stability, T ≥ 1400K.

Durchgeführte Arbeiten und erreichte Ergebnisse

1. High temperature thermoelectric properties of $LnCo_{1-x}(Ni, Ti)_xO_3$

The effects of Co-site and La-site substitution in the lanthanum cobaltate ($LaCoO_3$) may considerably improve its transport properties by changing the oxidation state of Co. It is possible to improve the Seebeck coefficient values for a low substitution level and to tune the sign of the Seebeck coefficient by suitable substitutions. We study the influence of partially substitution of the Co-site by Ti and Ni in the $LaCoO_3$ system [2,3].

The oxidation state of the Co ion in the $LaCo_{1-x}Ti_xO_3$ system is studied by Near edge X-ray absorption spectroscopy (XANES).

XANES measurements were performed at the Co K-edge at the beamline E4 at the Hamburger Synchrotron Radiation Laboratory, HASYLAB. Data were collected in transmission mode with the use of three ionization chambers filled with Nitrogen, the first one, and Argon for the second and the third one. The samples where placed between the first two detectors, and a Co-foil between the last two. The energy scale was calibrated from the first inflexion point in the Co K-edge (7.709 KeV). Spectra were aquired in 2 eV increments within the pre-edge region (7.50-7.69 KeV), 0.50 eV near the edge (7.69-7.75 KeV), and 1 eV within the region (7.75-7.78 KeV). CoO, $LaCoO_3$compounds were used as standards for Co^{+2} and Co^{+3} oxidation state respectivetly.

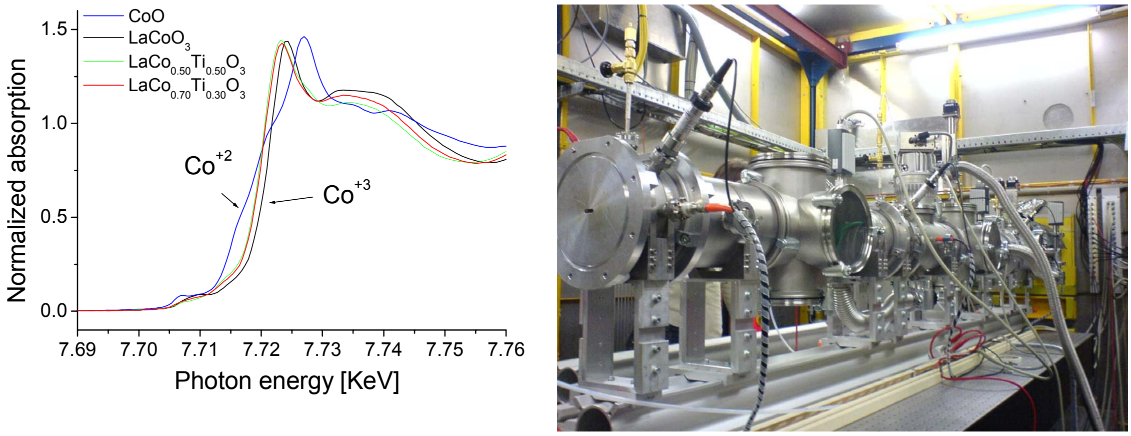

Figure 1. XANES spectra of the Co K-edge of CoO, $LaCoO_3$, $LaCo_{0.5}Ti_{0.5}O_3$ and $LaCo_{0.7}Ti_{0.3}O_3$ compound (left hand side). Image of the experimental set-up at HASYLAB (right hand side).

The Co K-edge XANES spectra for the compounds, CoO, $LaCoO_3$, $LaCo_{0.5}Ti_{0.5}O_3$ and $LaCo_{0.7}Ti_{0.3}O_3$, is shown in Figure 1. The Co K-edge threshold was determined from the first root in the first derivative of the near-edge region (XANES). The edge shift of the Co K absorption edge to higher or lower phonon energies with respect to 7.709 KeV gives information about the average valence of the Co. $LaCo_{0.5}Ti_{0.5}O_3$ and $LaCo_{0.7}Ti_{0.3}O_3$ shows a Co K-edge shifht to lower phonon energy with respect to $LaCoO_3$ which can be attribute to the presence of Co^{+2} ions in a Co^{+3} matrix.

The Seebeck coefficient of $LaCo_{0.98}Ni_{0.02}O_3$is positive indicating predominant charge carriers and has a value of S = + 360 μV/K at room temperature. A negative thermoelectric power is found in low level substituted $LaCo_{0.99}Ti_{0.01}O_3$. When Co^{3+} ions are substituted by Ti^{4+} ions in the $LaCoO_3$ system, Co^{2+} ions are generated, and negative charge carriers are introduced into the system. At low substitution level, two types of charge carriers may be present, but electrons are dominating at room temperature leading to a large negative Seebeck coefficient, see Figure 2a.

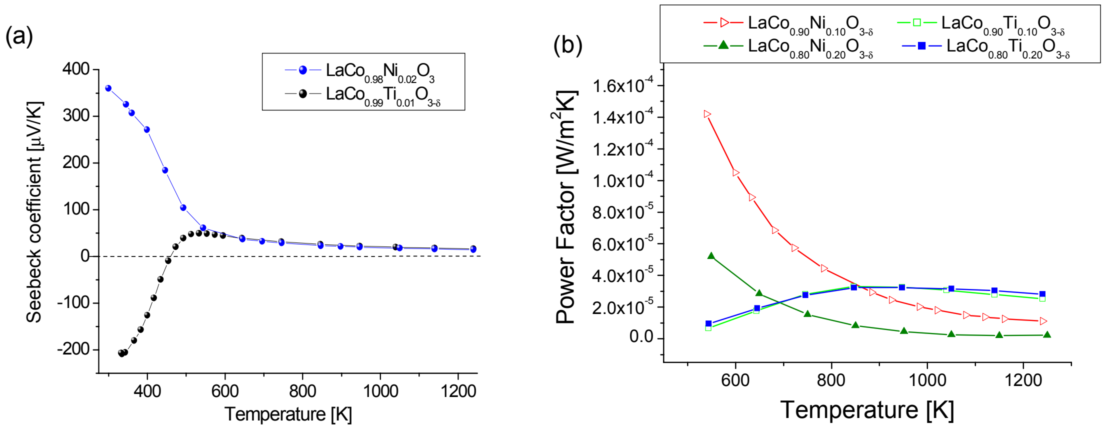

Figure 2. Temperature dependence of the Seebeck coefficient of $LaCo_{0.98}Ni_{0.2}O_3$ and $LaCo_{0.99}Ti_{0.01}O_3$ in the range of 340 K < T < 1240 K, (a), and Temperature dependence of the Power Factor of $LaCo_{1-x}(Ti,Ni)_xO_3$ (with x = 0.10, and 0.20) in the temperature range of 500 K < T < 1240K,(b).

The temperature dependence of the power factor ($PF = S^2*\sigma$) is presented in Figure 2b. The power factor (PF) of the Ni substituted compounds decreases with increasing temperature. However, the compound with x = 0.10 nickel content has a PF = $1.42*10^{-4}$ W/m^2*K at T = 540 K. On the other hand, the Ti substituted compounds exhibit an increase of the power factor with increasing temperature. Ti substitution leads to higher PF at T = 1240 K compared to that of Ni substituted compounds, e.g. PF($LaCo_{0.80}Ti_{0.20}O_3$) = $2.82*10^{-5}$ W/m^2*K and

PF($LaCo_{0.80}Ni_{0.20}O_3$) = $9.5*10^{-6}$ W/m^2*K at T = 1240K. It is interesting to investigate the possibility of these Ti substituted $LaCoO_3$ oxides to be used as high temperature thermoelectric materials since the PF increases with temperature.

2. Characterization of $LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$ (Ln = La, Pr, Nd, Sm, Gd) perovskite- type oxides:

The perovskite type-oxides are synthesised by a soft chemistry method based on the chelation of metals with citric acid in aqueous solution. Lower reaction temperature (T = 873 K) and two times shorter reaction cycles compared to ceramic methods allow the production of single phase metal oxides with various compositions and mesoporous morphology. The cationic composition, Co: Ni ratio is analysed for all samples by TEM/EDAX. The oxygen content is analysed by the hot gas extraction method using a LECO TC 500, see Table1.

Elemental composition	**Cationic composition / EDAX**		**Oxygen content**
	Co	**Ni**	**Hot-gas extraction**
La $Co_{0.95}Ni_{0.05}O_3$	0.95 ± 0.02	0.054 ± 0.01	2.95 ± 0.03
Pr $Co_{0.95}Ni_{0.05}O_3$	0.96	0.036 ± 0.01*	3.08 ± 0.04
Nd $Co_{0.95}Ni_{0.05}O_3$	0.93 ± 0.01	0.068 ± 0.01	2.99 ± 0.02
Sm $Co_{0.95}Ni_{0.05}O_3$	0.95 ± 0.01	0.053 ± 0.01	3.03 ± 0.02
Gd $Co_{0.95}Ni_{0.05}O_3$	0.96	0.041 ± 0.01	3.04 ± 0.02

Table 1: Composition thermoelectric cobaltate phases

The morphology of the calcinated product powders is analyzed using a LEO JSM-6300F scanning electron microscope (SEM) and a Phillips CM30 transmission electron microscope (TEM).The morphology studies on the powders heated at T = 873 K reveal a porous structure. The particles with an uniform particle size of approximately 70 nm diameter are partly agglomerated. After further annealing at T = 1273 K, the sintering processes lead to an increase of the crystallite size to a submicrometer level, see Figure 3.

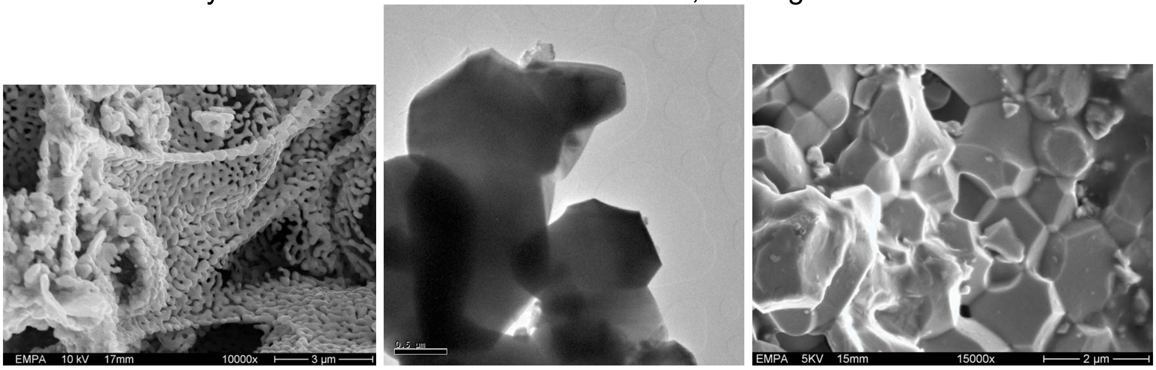

Figure 3. SEM and TEM micrograph pictures of powders with the composition $GdCo_{0.95}Ni_{0.05}O_3$ produced at 873 K (a), at 1273 K, (b), and sintered pellets at 1273 K, (c).

The structural analysis of the products was done using synchrotron powder x-ray diffraction (SPXD) facilities at HASYLAB/DESY, Hamburg, and the data refinement was performed with Rietveld procedure using FULLPROF program, see Figure 4.

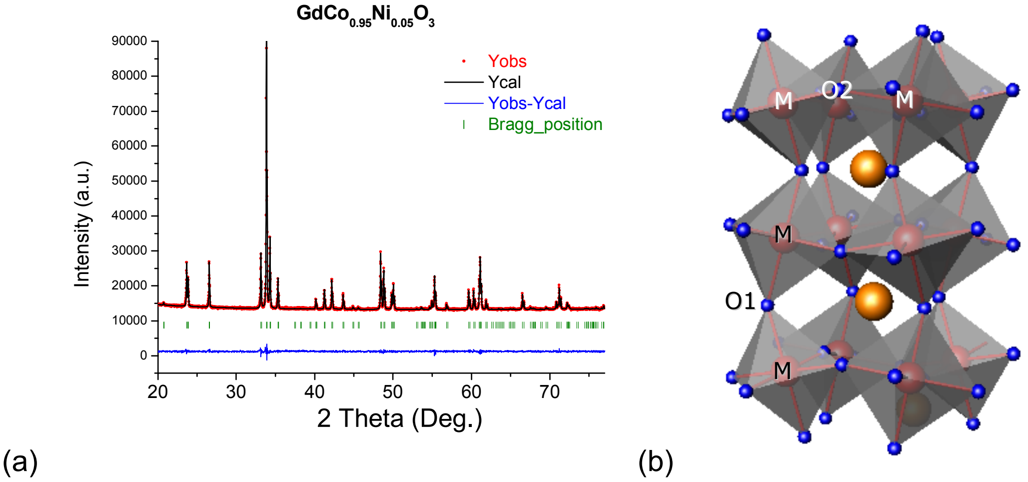

Figure 4. XRD pattern of $GdCo_{0.95}Ni_{0.05}O_{3+\delta}$, (a) and crystal structure representation, (b).

Analyzed powder X-ray diffraction data of $LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$ (Ln = La, Pr, Nd, Sm, Gd) reveal that all compositions are single-phase and crystallize in the orthorhombic crystal symmetry (space group Pbnm) for Ln = Pr, Nd, Sm, Gd, and Rhombohedral crystal symmetry (space group R3-c) for Ln = La.

The structure and microstructure studies were done by High resolution transmission electron microscopy (HREM) and electron diffraction (ED) in a Philips CM30, see Figure 5. HRTEM studies confirm highly crystalline and chemically homogeneous compounds.

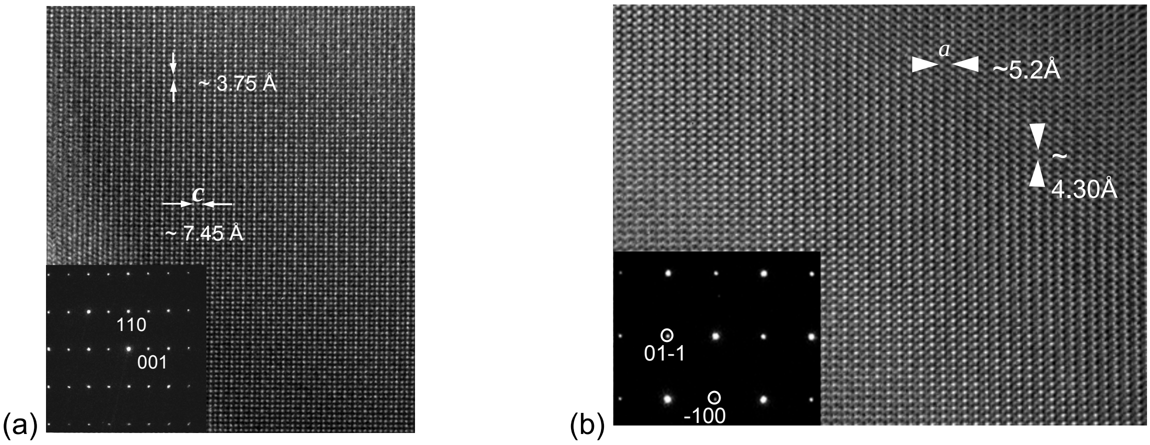

Figure 5. HRTEM micrograph of powders with the composition $GdCo_{0.95}Ni_{0.05}O_3$ produced at 873 K, zone axis [-110], (a), and zone axis [011].

The variation of the lanthanide ionic radii influences the crystal structure. While the $LaCo_{0.95}Ni_{0.05}O_{3-\delta}$ crystallized in rhombohedral crystal structure, the parent compounds with smaller rare-earth cations crystallized in orthorhombic crystal structure. The decrease of the lanthanide ionic radii ($Pr^{3+} > Nd^{3+} > Sm^{3+} > Gd^{3+}$) leads to a decrease of *a* and *c* lattice parameter and an increase of the *b* lattice parameter, see.Table 2, and thus to an increasing of the lattice distortion.

$LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$	*a* (Å)	*b*(Å)	*c*(Å)	angle (°)	
				M-O1-M	M-O2-M
La	5.447(1)	13.099(3)	5.447(1)		
Pr	5.384(7)	5.350(2)	7.588(4)	156.95	156.87
Nd	5.353(7)	5.344(4)	7.562(5)	161.52	155.84
Sm	5.294(7)	2.366(0)	7.511(6)	153.26	152.73
Gd	5.232(4)	5.408(6)	7.461(1)	149.65	152.73

Table 2. Lattice parameters and M-O-M angles of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln = La, Pr, Nd, Sm, Gd).

These structural changes influence the thermoelectric properties of the $LnCo_{0.95}Ni_{0.05}O_{3-\delta}$ system. The electrical resistivity data show correlation with the ionic radius of Ln cation in the $LnCo_{0.95}Ni_{0.05}O_3$ system [4]. The temperature of the semiconductor to metal transition is increasing with decreasing rare-earth ionic radii, see Figure 6a.

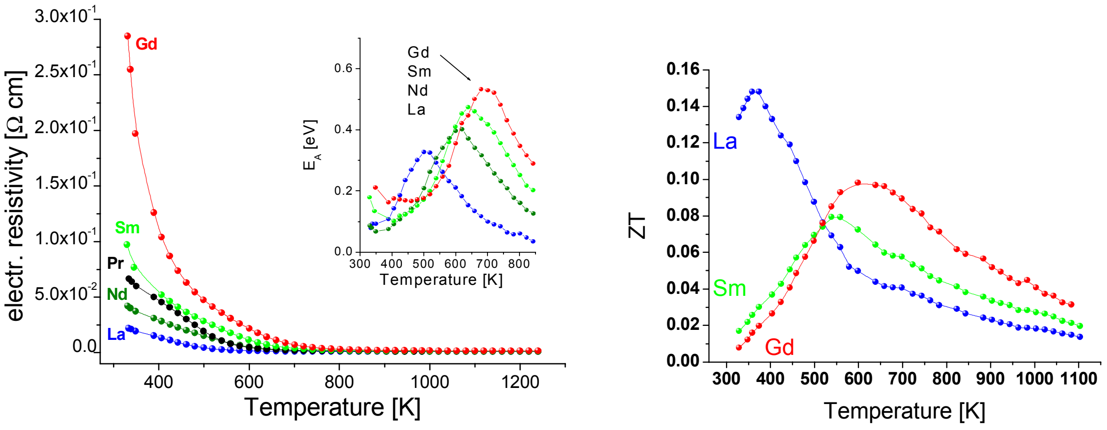

Figure 6. The temperature dependence of the electrical resistivity and the energy of activation (inset) of $LnCo_{0.95}Ni_{0.05}O_{3\pm\delta}$ (with Ln = La, Pr, Nd, Sm, and Gd), (a), and the temperature dependence of the figure of merit, ZT, (b).

3. Alternative Materials

Besides perovskite oxides other alternative high temperature thermoelectric materials were studied. Very promising due to their electronic structure are half-heusler compounds. Furthermore different chalcogenides and selenides are considered.

Nationale Zusammenarbeit

- Neutron diffraction (ND)and X-ray diffraction (XRD) experiments at SINQ and SLS
- Experiments with concentrated solar radiation are planned with A. Steinfeld, PSI.

Internationale Zusammenarbeit

- X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) experiments at HASYLAB/DESY, Hamburg.
- Half- heusler compounds, Prof. Dr. Claudia Felser, Uni Mainz.
- Selenides and Chalcogenides, Wolfgang Bensch, Uni Kiel

- Prof. Dr. Armin Reller, Uni Augsburg is the doctor father of the PhD candidate.

Bewertung 2007 und Ausblick 2007+1

The successful synthesis and characterization of the new ceramic thermoelectric materials led to several scientific publications and presentations so that the PhD finalization is envisaged for 2007.

Planned are further studies on single crystalline materials synthesized in a floating zone furnace and on epitaxial thin films.

Since the determination of the transition metal oxidation state and the crystallographic structure with exact anionic position of the new materials is crucial for understanding the structure-property-relations, further experimental campaigns are planned on large scale facilities starting in spring 2007.

The results will be finally used for a determination of composition-structure-property-relations in the system in 2008.

Referenzen

[1] D. M. Rowe, General Principles and Basic considerations. in Thermoelectrics handbook (ed. D.M. Rowe), Chap. 1, Taylor & Francis Group (2006).

[2] R. Robert, L. Bocher, B. Sipos, M. Döbeli, A. Weidenkaff, Prog. in Solid State Chem. (in press) (2006).

[3] R. Robert, L. Bocher, M. Trottmann, A. Reller, and A. Weidenkaff, Thermoelectric Ni substituted $LaCoO_3$ for solar energy conversion processes, *Journal of Solid State Chemistry,* 179 (2006) 3867-3873.

[4] R. Robert, M.H. Aguirre, G. Fortunato, P. Hug, A. Reller and A. Weidenkaff, in preparation.