Oxide materials development for solar thermoelectric power generators

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Abstract

Fine particles of the general composition $La_{1-x}Ca_xCoO_3$ ($0<x<0.4$) and $Ca_3Co_4O_9$ are produced as potential candidates for thermoelectric devices operating at high temperatures ($T>600$ K). A soft-chemistry method based on citrate precursors allows us to control the elemental composition from ppm level to 50% in these cobalt oxide systems in order to modify the Co valency and therefore the transport properties. The thermal decomposition of the precursors was studied by thermogravimetric analysis to determine the lowest temperature for the oxides synthesis. The prepared $Ca_3Co_4O_9$ phases show a thermopower value of $S_{300K} \approx 123\ \mu VK^{-1}$, and a resistivity of $\rho \approx 1.9$ mΩcm; . The 20% Ca-substituted $LaCoO_3$ show a Seebeck coefficient of $S_{300K} \approx 70\ \mu VK^{-1}$ and a resistivity of $\rho \approx 0.1$ Ωcm.

Introduction

The increasing demand on energy worldwide requires the use of new energy sources. The use of concentrated solar radiation as energy source is an attractive and environmentally clean way to generate electrical power {Wu, 1996 #2084}, see fig. 1.

The direct efficient thermoelectric conversion of solar heat into electricity requires the development of novel functional materials exhibiting large electrical conductivity, large Seebeck coefficient and small thermal conductivity with high thermal and chemical stability at high temperature. Since these transport properties are interrelated, the development of a material breaking this relationship is a great challenge [1-3].

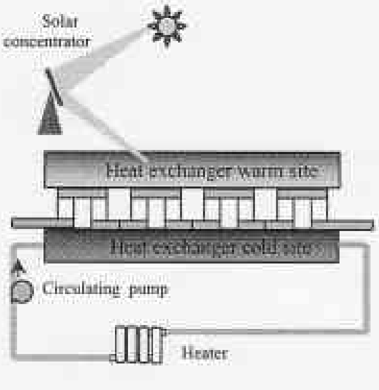

Figure 1. Thermoelectric diagram for solar power generators.

Since the discovery in 1997 of the large thermopower S close to 100µV/K at room temperature in the metallic $NaCo_2O_4$ layered oxide [4], metal oxides have been recognized as good candidates for thermoelectric (TE) applications at high temperature to compete with conventional TE materials due to their high thermal and chemical stability.

Among a wide range of potential candidates for thermoelectric applications, we selected nanostructured 2-D and 3-D oxides since dimensionality is an important parameter to modify the figure of merit $Z=S^2/\rho\kappa$ [5-7].

Soft chemistry synthesis approaches are very suitable for the production of the complex transition metal oxide phases, because they allow the production of high surface area compounds with diverse compositions which can not be obtained by classical solid state chemistry synthesis routes.

Perovskite-type phases show a variety of useful properties and a high potential for energy conversion processes [8, 9]. Depending on their composition they reveal insolating, p- or n-type semiconducting, metallic or even superconducting transport properties. In the lanthanum cobaltite phases, the effects of Co-site and A-site substitution may improve its thermoelectric properties by changing the oxidation state of Co. In Sr-doped $LaCoO_3$ the values of S reached up to +300-600 µV/K at 300K [10]. The present work is focused on the synthesis methods for high surface area $La_{1-x}Ca_xCoO_3$ ($0< x< 0.4$), and "misfit cobaltite" $Ca_3Co_4O_9$, the study of the influence of the precursor polymerisation, and finally, the effect on the physical properties of the compounds.

Experimental

$La_{1-x}Ca_xCoO_3$ ($0<x<0.4$), and the "misfit cobaltite", $Ca_3Co_4O_9$, were obtained by thermal decomposition of the corresponding amorphous citrate precursor. The citrate precursor were prepared by dissolving an appropriate amount of citric acid (CA) monohydrate, $La(NO_3)_3{*}6H_2O$, $Ca(NO_3)_2{*}4H_2O$ and $Co(NO_3)_2{*}6H_2O$ (Merck, purity ≥ 98%) in water under continuous stirring, for at least 24 h at room temperature to obtain La,Ca- and Co-CA complexes. A small amount of ammonia solution was added to adjust the pH of the precursor solution to pH < 4 or pH >4, respectively. The clear, and intense pink solutions were dried using a rotary evaporator (T= 60°C, p= 20mbar) resulting in a xerogel. The xerogel was pre-decomposed at 300°C to result in a voluminous product which was then milled and calcinated at 600°C in ambient atmosphere for 6h to obtain the $La_{1-x}Ca_xCoO_3$ phases or heated to 700°C to obtain the misfit cobaltite, $Ca_3Co_4O_9$.

The thermal decomposition of the different precursors was analyzed by thermogravimetric analysis (TGA) using a Netzsch STA 409 CD system to monitor a thermogravimetric (TG) and a differential thermal analysis (DTA) signal. The structural analysis of the products was done by using X-ray diffraction (XRD) data collected on a Bruker D500 diffractometer with Cu-K_α radiation. The morphology of the calcined powder was analyzed using a LEO JSM-6300F scanning electron microscope (SEM). The elemental composition was analyzed using an energy dispersive X-ray analysis (EDX) detector system coupled to the SEM. Transmission electron microscopic (TEM) studies were done on a Phillips CM 30 instrument.

The transport properties have been measured using a Physical Properties Measurements System (PPMS) between 2K and 400K. The electrical resistivity (ρ) is measured by the four probe technique with indium contacts deposited with ultrasonic waves. The thermopower (S) was measured by a steady-state technique. The thermopower (S) have also been measured at $300K < T < 600K$ in a self-made set-up [11] based on Stölzer et al. [12].

Results and Discussion

In the applied soft chemistry processes the complex oxides are formed in a combustion process of tailor-made complex precursors containing a premix of the cations on a molecular level [13, 14]. In these modified so called "pecchini" processes citrates precursors are used [15]. The advantage of using citric acid as ligand is the formation of stable complexes with many cations.

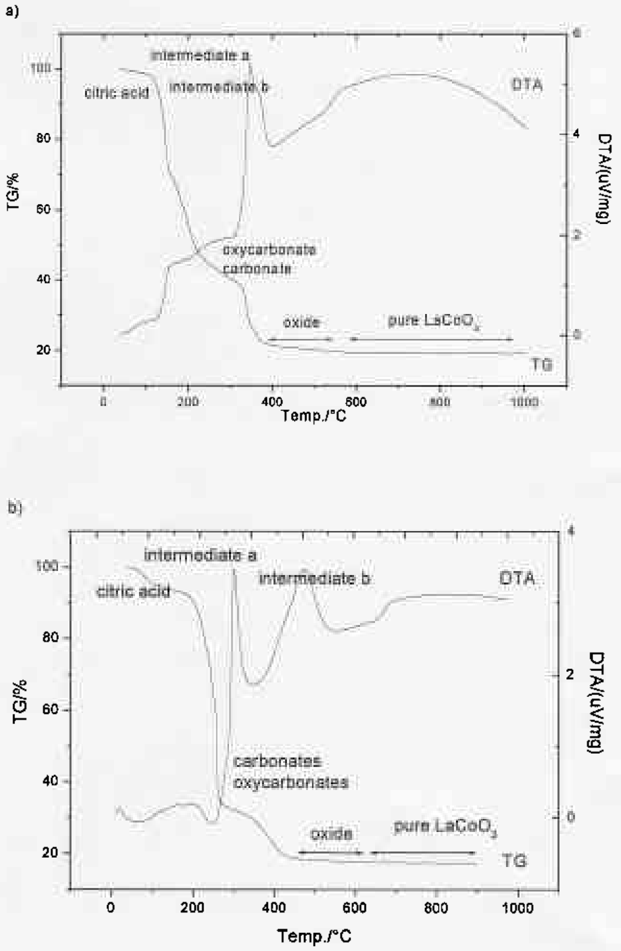

Figure 2. Thermogravimetric data for the decomposition of the La-Ca-Co-citrate precursors. a) citrate precursor at pH < 4, and b) citrate precursor at pH > 4.

To study the formation of the oxide from the precursor, different decomposition experiments were carried out in a thermobalance. The samples were heated to 900°C with a heating rate of 4 K/min. Figure 2 shows the TG and DTA curves of the phase formation process from the precursor derived at pH< 4 (a) and at pH> 4 (b), respectively. At a relatively low temperature of 160°C, the excess of citric acid is decomposed resulting in a weight loss of 29.38% in the gel formed at pH< 4 and 6.32% of weight loss in the gel formed at pH> 4. The thermal decomposition of the La-Ca-Co-citrate precursor and oxide phase formation occurs in two well defined steps. For the acidic precursor the decomposition starts at 265°C while the non-acidic precursor shows slightly varied behaviour, the precursor decomposition occurs at higher temperature of 330°C, which is probably due to a modified precursor structure. In both citrate-precursor routes the pure oxide is obtained at 600°C.

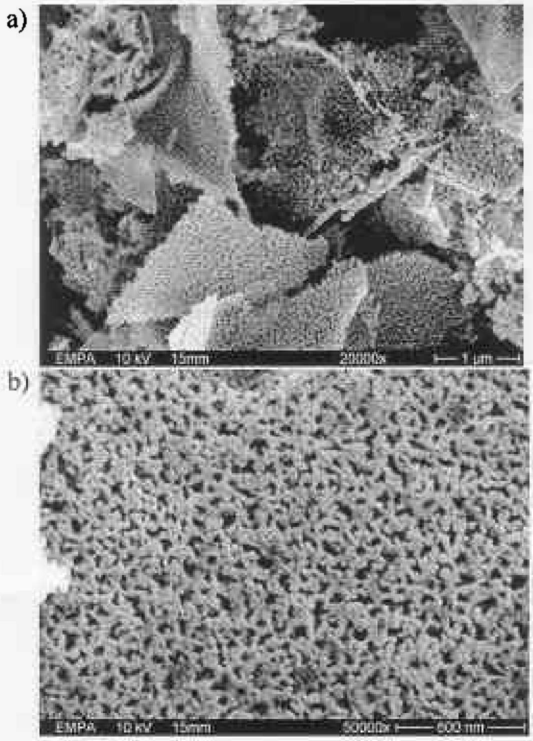

Figure 3. SEM micrograph pictures of powders synthesized by the citrate method, (a) $LaCoO_3$ product, and b) $La_{0.9}Ca_{0.1}CoO_3$ product.

Figure 3 shows the microstructure of the $LaCoO_3$ (a) and of $La_{0.9}Ca_{0.1}CoO_3$ (b). In both cases the particle size is in the nano-scale range and both SEM micrographs show uniform grain size distribution, between 48 and 60 nm diameter for $LaCoO_3$ particles and between 14 and 18 nm diameter for $La_{0.9}Ca_{0.1}CoO_3$ particles. The $LaCoO_3$ particles are compacted in triangular-shaped layers, while the $La_{0.9}Ca_{0.1}CoO_3$ particles are forming a porous microstructure. $LaCoO_3$ perovskite has been obtained from a precursor solution at pH< 4 while $La_{0.9}Ca_{0.1}CoO_3$ perovskite results from a precursor solution at pH> 4. From the morphological point of view, there is a significant difference between the particles size depending on pH and composition of the starting citrate precursor. The products show typically a surface area of 10-30 m^2/g.

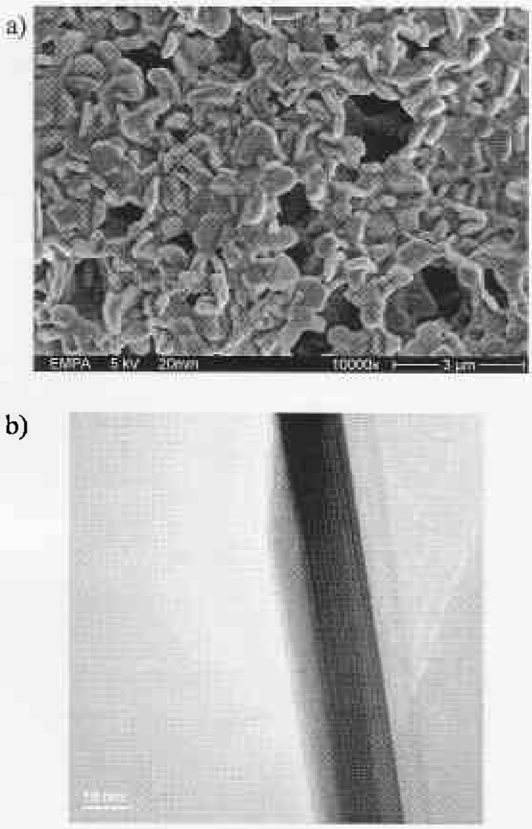

Figure 4. a) SEM micrograph of $Ca_3Co_4O_9$ powders synthesized by the citrate method, and b) cross sectional TEM view of the 2D-structure of the thin platelets.

The misfit $Ca_3Co_4O_9$ prepared from a citrate precursor at pH<4 posses platelet-like shaped particles of 370 and 820 nm diameter (fig. 4a). The individual particles are compacted to a porous microstructure. HRTEM images (b) reveal the layered 2D-structure of the "misfit" structure.

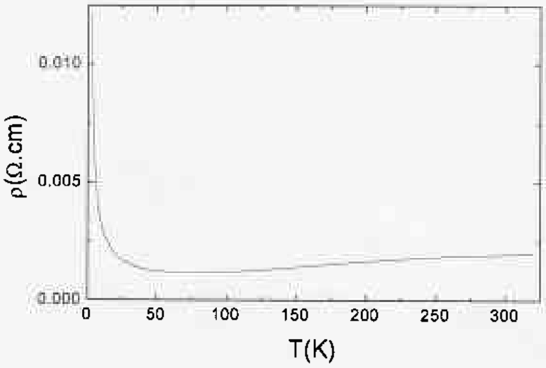

Figure 5. Temperature dependence of electrical resistivity of $Ca_3Co_4O_9$.

The electrical resistivity (ρ) versus temperature of $Ca_3Co_4O_9$ in the range of 0K to 300K is presented in figure 5. The ρ-T curve shows metallic-like behaviour (i.e. dρ/dT>0) below 20K while semiconducting-like behaviour (i.e. d ρ/dT<0) above 20K. The resistivity presents a minimum value of 1.15 mΩcm between 70 and 80K.

The temperature dependence of the thermopower (S) is presented in figure 6. The thermoelectric values are positive, indicating p-type conduction. The Seebeck coefficient at room temperature is 123 μVK^{-1} and increases with increasing temperature until achieving a value of 163 μVK^{-1} at 580 K. The value obtained at 300K is similar to the reported value for single crystals [16].

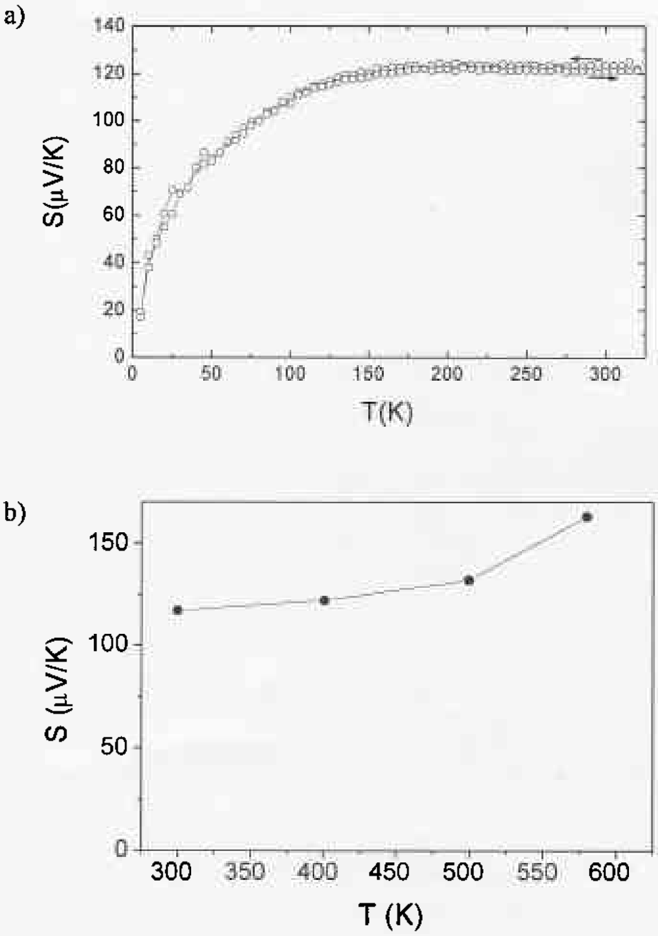

Figure 6. Thermopower measurements of $Ca_3Co_4O_9$ at low temperature (a) and High temperature (b).

Figure 7 (a) shows temperature dependences of ρ for $La_{1-x}Ca_xCoO_3$ (0<x<0.4) observed in the temperature range between 2 and 300K. The measurements show a typical semiconductor conduction behaviour of the cobaltate compounds. The conductivity increases as expected with increasing Ca^{2+} substitution [17], because mobile oxygen vacancies as well as Co^{4+} ions are induced through substitution of the La^{3+} by Ca^{2+}.

The increased conductivity of the highly substituted compounds can be explained by enhanced charge carrier mobility in the presence of a higher Co^{4+} content. As increasing the content of Co^{4+} the resistivity decreases to a value of 0.1 Ω cm for x = 0.4.

Fig. 7 (b) shows the temperature dependent variation of the thermopower for $La_{0.8}Ca_{0.2}CoO_3$. The value of S of the Ca-substituted $LaCoO_3$ is ≈ 70 μVK^{-1} at 300K.

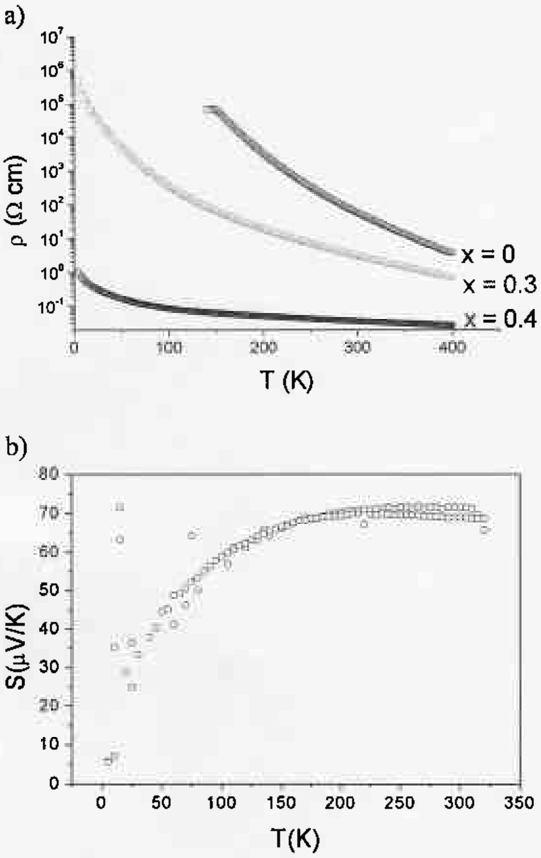

Figure 7. Resistivity data for $La_{1-x}Ca_xCoO_3$ (0<x<0.4),(a), and thermopower data for $La_{0.8}Ca_{0.2}CoO_3$, (b).

Conclusions

$La_{1-x}Ca_xCoO_3$ (0<x<0.4) and $Ca_3Co_4O_9$ single phase products have been successfully syntesized by a soft-chemistry process. The pH of the precursors have a substantial influence on the morphology of the products. Although all the precursors lead to fine particles, the product derived from the polymeric precursor shows the smallest particle diameter. Moreover, the morphology is also influenced by the cationic composition of the precursor. Higher Ca content leads to larger particle diameter.

The substitution of Ca for La in the 3D-compound decrease the resistivity down to a value of 0.1 Ω cm for x = 0.4. The value of S of the Ca-substituted $LaCoO_3$ is ≈ 70 μVK^{-1} at 300K.

The misfit cobaltite $Ca_3Co_4O_9$ has a Seebeck coefficient at room temperature of 123 μVK^{-1}, similar to the reported value for single crystals which's S increases with T to a value of 163 μVK^{-1} at 580 K. The resistivity presents a minimum value of 1.15m Ω cm between 70 and 80K.

The citrate method is a promising process for the synthesis of complex oxides. The advantages offered by this method, compared to the ceramic method, are low synthesis temperature, homogeneous microstructure of the produced powder and control of the elemental composition from ppm level to 50%. The similar transport properties compared to coarse particles products, i.e. the misfit cobaltite, drive us to further investigation.

Acknowledgments

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