ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT

Journal of Solid State Chemistry 178 (2005) 769–775

JOURNAL OF
SOLID STATE
CHEMISTRY

www.elsevier.com/locate/jssc

Partial substitution of rhodium for cobalt in the misfit $[Pb_{0.7}Co_{0.4}Sr_{1.9}O_3]^{RS}[CoO_2]_{1.8}$ oxide

Denis Pelloquin, Sylvie Hébert, Antoine Maignan[*], Bernard Raveau

Laboratoire CRISMAT, UMR CNRS-ENSICAEN 6508, 6 boulvard du Maréchal Juin, 14050 Caen Cedex, France

Received 31 July 2004; received in revised form 15 November 2004; accepted 19 November 2004

Abstract

The partial substitution of Co by Rh in the $[Pb_{0.7}Co_{0.4}Sr_{1.9}O_3]^{RS}[CoO_2]_{1.8}$ family has been investigated. By transmission electron microscopy and X-ray powder diffraction, it is shown that the substitution of Rh for Co takes place at the two cobalt sites of the structure but for the low enough Rh contents, this substitution is made preferentially at the level of the CdI_2-like layer. Thus, a generic formula $[Pb_{0.7}(Co_{0.4-z}Rh_z)Sr_{1.9}O_3]^{RS}[Co_{1-y}Rh_yO_2]_{b1/b2}$ $(0\leqslant y\leqslant 0.5$ and $0\leqslant z\leqslant 0.3)$ can be proposed for this new family of misfit phase. As observed for the pure misfit cobaltite, the thermoelectric power is also very large, close to +140 μV/K at room temperature. The Rh cation can adopt a mixed valency Rh^{3+}/Rh^{4+} ($4d^6/4d^5$) with low spin states t_{2g}^6/t_{2g}^5 equivalent to the ones of low spin Co^{3+}/Co^{4+} ($3d^6/3d^5$). The large thermopower observed in the Rh substituted compounds is therefore a direct proof that the coexistence of low spin states t_{2g}^6/t_{2g}^5 contributes to the thermoelectric power enhancement in these oxides.

Keywords: Cobalt oxide; Thermopower; Rhodium oxide

1. Introduction

The intensive research in the cobalt oxides points out to the great ability of the cobalt species to adopt a mixed valence state and various spin state configurations in different basic structural environments, such as perovskite or CdI_2-type blocks. This richness allows to design some new structural frameworks with interesting physical properties. Among the latter, the thermoelectric properties have been the focus of numerous studies these last years after the discovery of a high thermoelectric power (~100 μV/K at 300 K) and a low resistivity (~200 μΩ cm at 300 K) in $NaCo_2O_4$ [1]. The research for new thermoelectric materials operating at high temperatures ($T\gg 300$ K) is a very interesting challenge since the waste heat conversion into electrical energy is economical and non-polluting. Recently a large oxide series which exhibits hexagonal Co sheets of the CdI_2-type containing edge-shared CoO_6 octahedra—similar to that of $NaCo_2O_4$ [1]—interleaved with three or four rocksalt (RS) type layers has been isolated. These materials, the so-called "misfit" cobaltites due to their aperiodic composite feature, can be described by the generic formula $[(A'_{1-x}Co_y)_{n-2}A_{2+x-y}O_n]^{RS}[CoO_2]_{b1/b2}$ in which n is the number of RS-type layers ($n=3$ or 4 and $A'=$ Co,Bi, … and $A=$ Ca, Sr) [2–7] and the b_1/b_2 ratio represents the incommensurate ratio of the b parameters of the two subcells.

One possible origin for the large Seebeck coefficient of Na_xCoO_2 is based on the different valencies and spin states the cobalt species can adopt [8]. In the limit of high temperature, the thermopower can be estimated from a generalized Heikes formula, which takes into account the carrier density as well as their spin degeneracy (low spin, intermediate spin or high spin). A mixture of low spin Co^{3+} and low spin Co^{4+} (t_{2g}^6/t_{2g}^5) was proposed to be at the origin of the large thermoelectric power observed at high temperature in Na_xCoO_2. For misfit cobaltites, the same explanation can be given to explain their good thermoelectric properties and the improvement that can be achieved by different

---

[*] Corresponding author. Fax: +33 2 31 95 16 00.
E-mail address: antoine.maignan@ensicaen.fr (A. Maignan).

0022-4596/$ - see front matter
doi:10.1016/j.jssc.2004.11.021

substitutions [9]. By magnetic measurements [4] and photoemission studies [10], the coexistence of low spin Co^{3+}/low spin Co^{4+} in the CoO_2 layers has been proposed. One way to demonstrate the importance of the mixture of low spin Co^{3+}/low spin Co^{4+} to achieve large Seebeck coefficient is by substituting an isoelectronic element for Co in the CoO_2 layer.

The difficulty with substitution in misfit cobaltites is that two different Co sites can be substituted, in the RS layers or in the CoO_2 layers. Recently, different substitutions at the level of RS layers have been reported in such type of oxides. In particular, the strontium substitution for calcium in $Ca_3Co_4O_9$, namely $[Co\,Ca_2O_3]^{RS}[CoO_2]_{1.62}$, has been made [11,12] and the possibility to introduce partially lead [9,13], mercury [13,14] or lanthanides [15] instead of cobalt in the rock–salt type layers has been demonstrated. By this way a significant enhancement of the RT thermopower has been reported in $[Pb_{0.4}Co_{0.6}Ca_2O_3]^{RS}[CoO_2]_{1.61}$ with the highest value of 165 μV/K [9]. The substitutions reported with transition elements has led to the synthesis of $[Ti_{0.4}Co_{0.6}Ca_2O_3][CoO_2]_{1.62}$ [16] and $[Ca_2(Co_{0.65}Cu_{0.35})_2O_4][CoO_2]_{1.60}$ [17], two new $n=3$ and 4 misfit cobaltites, respectively. All copper or titanium species are located in the RS-type subcell and do not directly modify the conducting $[CoO_2]$-type CdI_2 layers.

In the case of $NaCo_2O_4$, substitutions with Cu [18], Pd [19] or Mn [20] for Co have been reported. Even if the physical properties are modified, no definite proof that the substitution takes place only in the CoO_2 layer has been given.

A new attempt to modify the CoO_2 layers in misfit cobalt oxides is presented here. According to a similar filling of the d orbitals for $Co^{3+/4+}$ ($3d^6$,$3d^5$) and $Rh^{3+/4+}$ ($4d^6$,$4d^5$) and to the stability of the low spin state of the latter [21], the rhodium species appear to be a promising candidate to substitute the cobalt species. Here we report on different levels of rhodium substitution for cobalt in the lead-based $[Pb_{0.7}Co_{0.4}Sr_{1.9}O_3]^{RS}[CoO_2]_{1.8}$ misfit cobaltite. The structural characterizations by transmission electron microscopy (Electron Diffraction + Energy Dispersive Spectroscopy) and powder X-ray diffraction data are reported and evidence large rhodium substitution for cobalt. Such analytical results imply the partial substitution of cobalt species sitting in the CdI_2-type layers. The thermopower properties are given and compared with the previously reported pure $[(A'_{1x}Co_y)_{n-2}A_{2+x-y}O_n]^{RS}[CoO_2]_{b1/b2}$ cobaltites. The large thermoelectric power values emphasize the importance of low spin Co^{3+}/Co^{4+} mixture in the CoO_2 layers to achieve large Seebeck coefficients.

2. Experimental

The synthesis of the polycrystalline samples is similar to the method used in the case of Pb-based misfit cobaltites [9,13]. Stoichiometric amounts of oxides and peroxides, Rh_2O_3, PbO, SrO_2 and Co_3O_4 are weighted according to the nominal cation composition $Pb_{0.7}Sr_{1.9}Co_{2.2-x}Rh_xO_y$, deduced from the structural study of the pure cobalt $[Pb_{0.7}Co_{0.4}Sr_{1.9}O_3]^{RS}[CoO_2]_{1.8}$ oxide. Note that the Rh_2O_3 oxide is kept for one night at 1000 °C to avoid the presence of water molecules. Then the precursors are mixed and pressed in the form of bars. The samples are placed in silica tubes sealed under vacuum with approximately 0.8 g of sample for a volume of 3 cm^3 in the tube. The samples are heated up to 1000 °C with a heating rate of 150 °C/h, maintained at this temperature for 24 h and cooled down to room temperature at the same cooling rate. By this way, pressure is observed inside the tubes and black ceramic bars are obtained.

Next the as-prepared samples are analyzed by means of transmission electron microscopy (TEM) techniques. The electron diffraction (ED) analysis has been carried out using a JEOL 200CX microscope fitted with an eucentric goniometer (±60°) and equipped with KEVEX Energy Dispersive Spectroscopy (EDS) analyzer. The accuracy of this analysis technique is about 5/100 for each cation.

X-ray diffraction data are collected at room temperature using an XpertPro Philips vertical diffractometer working with the Cu$K\alpha$ radiation and equipped with a secondary graphite monochromator. Data collection is carried out by continuous scanning (step = 0.02° (2θ), preset = 10 s) over an angular range $5^\circ \leqslant 2\theta \leqslant 80^\circ$. Lattice constants and structural calculations were refined by the Rietveld method using the computer programs JANA2000 [22] and FULLPROF [23], respectively.

The magnetic properties are studied using a SQUID magnetometer (ac and dc; 0–5 T; 1.8–400 K). Resistance data as a function of temperature (1.8–400 K) or magnetic field (0–7 T) are collected with a Quantum Design physical properties measurement system (PPMS) by the four-probe technique. Current and voltage indium contacts are ultrasonically deposited on the sintered bars (typically 2 × 2 × 10 mm). A steady state method is used to measure the Seebeck effect (S) in the PPMS with high temperature limit fixed at 320 K by the calibration range of the temperature sensors.

3. Structural analysis

The samples have been prepared on the basis of the chemical formula previously reported for the Pb-based misfit oxide, $[Pb_{0.7}Co_{0.4}Sr_{1.9}O_3]^{RS}[CoO_2]_{1.8}$ [13]. In order to simplify this formula, especially if one takes into account that the location of the Rh cations in the RS and/or the CdI_2 type layers is a priori unknown, the formula can be written $Pb_{0.7}Sr_{1.9}Co_{2.2}O_{6.6}$. A series of