



Phase equilibria in Ca–Co–O system

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ABSTRACT

The phase equilibria in the ternary Ca–Co–O system have been studied by thermal analysis (DSC/DTA, TGA), X-ray diffraction of quenched samples and low temperature heat capacity measurements. These experimental data were combined with the data available in literature and used to assess the thermodynamic quantities of the involved phases. A particular focus was put on the misfit cobaltite $\text{Ca}_3\text{Co}_{3.93}\text{O}_{9.36}$ as a potential candidate for high temperature thermoelectric conversion whose observed nonstoichiometry was described in terms of compound energy formalism. The phase diagram was mapped using *FactSage* program.

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1. Introduction

Due to the lack of fossil fuels and risks connected with nuclear energy recently manifested by the accident in the Japanese nuclear power plant, energy recovery is becoming extremely important [1]. In this context the thermoelectric energy recovery from waste heat is recognized as a promising technology suitable for direct electric power generation [2]. More concretely, oxide materials recently attracted a great attention due to their ability to generate thermoelectric power at high temperatures without the risk to be decomposed and/or degraded by corrosion [3].

Within oxide thermoelectric materials family the misfit layer cobaltites are intensively studied, in particular due to their ability to be used in thermoelectric devices operating at elevated temperatures in oxidizing conditions [4]. Their structures, which are based on the $[\text{CoO}_2]$ hexagonal layers formed by the edge sharing CoO_6 octahedra interleaved between rock-salt type slabs, were in detail described by Lambert et al. [5]. Since at least one lattice parameter is different in these two types of structural units, the resulting stoichiometric coefficients are nonintegers even though the structures are perfectly ordered. The typical representatives $\text{Ca}_3\text{Co}_{3.93}\text{O}_{9.36}$ and $\text{Bi}_2\text{Sr}_2\text{Co}_{1.82}\text{O}_{7.64}$ can thus be expressed in terms of crystal chemical formulas $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$ and $[\text{Bi}_2\text{Sr}_2\text{O}_3][\text{CoO}_2]_{1.82}$, respectively [6]. All misfit cobaltites exhibit a positive Seebeck coefficient exceeding $100 \mu\text{V}/\text{K}$ (at room temperature), which moreover further increases with increasing temperature and can

thus constitute one pole of a thermoelectric uni-couple forming a key element of the thermoelectric battery [7].

One of the most promising application fields of such high temperature thermoelectric batteries is their application on the vehicular exhaust pipe, which being warmed up to 700°C offer a large potential for the recuperation of high graded waste heat [8].

Due to the fact that the primary aim in the optimization of thermoelectric properties of thermoelectric materials is motivated by the increase of the thermoelectric figure of merit $ZT = \alpha^2/(\lambda\rho)$, i.e. the material should simultaneously exhibit high thermopower α , low electrical resistivity ρ and low thermal conductivity λ , the interest of material scientists is focused on the increase of thermopower. This characteristics, being largely predetermined by the electronic structure and character of charge carriers in the vicinity of Fermi level, can be modified for instance by tuning Fermi level through chemical substitutions. That is the reason why a number of studies in recent years has been devoted to homovalent and heterovalent substitutions in misfit cobaltites, see e.g. [9]. On the other hand the electrical resistivity and thermal conductivity, being already decisively influenced by the scattering resulting from unmatched building structural units, are due to their percolation nature influenced by material microstructure.

No less importance than the optimization of the figure of merit ZT the chemical stability of the thermoelectric material with respect to partial or complete decomposition as well as to corrosion represents an equally important issue, namely in case of high temperature applications [3]. It follows that the knowledge of the respective phase diagram describing the pertinent phase stoichiometry and stability is crucial for proper optimization and tailoring of a given thermoelectric material and for its safe operation, as demonstrated e.g. on Zn_4Sb_3 [10]. The effect of synthesis

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conditions on the resulting properties of $\text{Ca}_3\text{Co}_{3.93}\text{O}_{9+\delta}$ misfit cobaltite has been recently demonstrated on the comparison of samples prepared by spark plasma sintering (reducing conditions) and by standard ceramic procedure in oxygen atmosphere [11].

In this study we thus focus on the assessment of the Ca–Co–O phase diagram based on both our and literature experimental data [12–17]. Since the system under study should be considered as closed for Ca and Co while open for oxygen which is exchanged with the surrounding atmosphere and whose content is determined and controlled by the oxygen activity in surroundings, the phase diagram is represented by means of three experimentally adjustable predictors - temperature, cation composition and oxygen activity (partial pressure). A particular attention is paid to a thermodynamic description of the experimentally determined cation and oxygen non-stoichiometry of the misfit phase $\text{Ca}_3\text{Co}_{3.93+x}\text{O}_{9+\delta}$. On the other hand, the second ternary oxide, $\text{Ca}_3\text{Co}_2\text{O}_6$, with a quasi-one-dimensional columnar structure built of alternating face-shared CoO_6 octahedra and trigonal prisms [18] is considered as purely stoichiometric.

2. Experiment and calculation

Samples with different Ca/Co stoichiometries were prepared by standard ceramic route starting from CaCO_3 (Aldrich, ACS) and Co_2O_3 (Riedel-de Haën, ACS) powders (both analyzed to determine the real contents of metallic components) mixed in appropriate stoichiometric rates (Ca/Co = 7/3, 3/2, 1/1, 1/2, 1/4, and five compositions in a close vicinity of the ideal stoichiometry 3/3.93 of the misfit phase, namely Ca/Co = 3/3.7, 3/3.8, 3/3.9, 3/3.95, 3/4 and 3/4.1). The starting mixtures were homogenized and calcined in air atmosphere at 850 °C and 900 °C for 24 h at each temperature. The calcined powders were pressed into pellets (uniaxial pressure 500 MPa) and sintered at 940 °C in O_2 atmosphere for 100 h in Pt vessels.

The phase composition of the multiphase samples and the structure parameters of misfit structure obtained in a form of single phase samples were evaluated from powder XRD patterns recorded within the range $2\theta = 2\text{--}80^\circ$ on X'Pert PRO diffractometer in Bragg–Brentano parafocusing geometry using $\text{CuK}\alpha$ radiation. The JANA program [19] for Rietveld refinement of incommensurate structures was employed to determine the lattice parameters including the misfit ratio of the $\text{Ca}_3\text{Co}_{3.93+x}\text{O}_{9+\delta}$ structure using the structure model (space group and the atomic positions) as proposed and confirmed by Lambert et al. [5]. The refinement quality is characterized by typical values of the obtained R-factors 0.1–0.2 and the average relative error of the refined lattice parameters 0.02%. An example of XRD pattern recorded on a single phase sample with the ideal composition $\text{Ca}_3\text{Co}_{3.93}\text{O}_{9+\delta}$ and the obtained Rietveld refinement profile is shown in Fig. 1.

The low temperature heat capacity of the misfit cobaltite was measured on the *Physical Properties Measurement System (PPMS)*, Quantum Design using a two relaxation time method on a ceramic sample with a mass of 30 mg and a relative density 72%. An adenda associated with the sample holder and the Apiezon cryogenic grease applied to attach the sample was determined over the entire temperature range (2–300 K) prior to the respective sample run. The measurements were performed with fully automatic procedure under high vacuum (pressure 10^{-2} Pa) to avoid the heat loss through the exchange gas.

The differential scanning calorimetry (DSC) measurements were performed on *Netsch DSC 404 C Pegasus* calorimeter at a heating rate 10 K/min in the dynamic oxygen and purified air atmosphere within the temperature range 20–1130 °C. The measured temperature was calibrated on the melting points of pure metal standards. For the heat capacity determination the apparatus

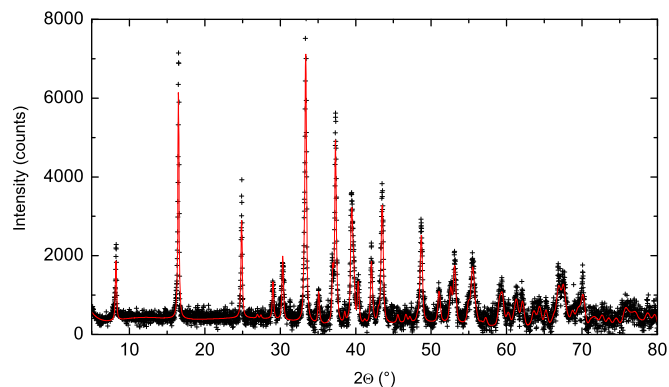


Fig. 1. X-ray powder diffraction pattern of the misfit cobaltite $\text{Ca}_3\text{Co}_{3.93}\text{O}_{9.2}$ and the obtained Rietveld refinement profile (solid line).

sensitivity was obtained as a function of temperature by measuring the sapphire standard (NIST, ref. N°720) under the same experimental conditions. Both the sample and standard signals were corrected by subtracting the signal of a blank sample crucible. The reference crucible was held empty during all experiments.

The oxygen stoichiometry of the misfit cobaltite was studied by thermogravimetric analysis (TGA) performed on Setaram STA instrument, model Setsys Evolution with a heating rate 10 K/min in air atmosphere.

The calculations of phase equilibria and the construction of phase diagrams were carried out by means of the *FactSage* thermochemical software and databases [20], version 6.1.

3. Thermodynamic models

The thermodynamic models of stoichiometric phases ($\text{Ca}_3\text{Co}_2\text{O}_6$, Co_3O_4 and $\text{Ca}_3\text{Co}_4\text{O}_{9.2}$ considered as a stoichiometric misfit phase in the first approximation) and end-members of solution phases ($\text{CaO}(s,l)$, $\text{CoO}(s,l)$, $\text{Co}(l)$ and $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3}$) are based on standard enthalpies of formation and entropies referred to ambient temperature $T=298$ K, and on the temperature dependence of heat capacity in a polynomial form, which are stored in *FactSage Compound* database format and serve as source data for calculation of Gibbs free energies. In the case of high temperature polymorphs the enthalpies and temperatures of phase transitions from the low temperature forms are used in place of enthalpies of formation and entropies.

The Gibbs energy of all solution phases is expressed in a standard way,

$$G^\phi = \sum_i (y_i G_i^\circ) - T \Delta S^{\text{id}} + \Delta G^{\text{ex}}, \quad (1)$$

as a sum of Gibbs energies of the involved species G_i° , the ideal mixing entropy term and the excess Gibbs energy considered in the Redlich–Kister (R–K) polynomial form

$$\Delta G^{\text{ex}} = y_M y_N \sum_j L_{j(M,N)} (y_M - y_N)^j, \quad (2)$$

for the liquid phase and the rock-salt type solid solution $\text{Ca}_{1-x}\text{Co}_x\text{O}$ with $\text{CaO}(l,s)$, $\text{CoO}(l,s)$ and $\text{Co}(l)$ representing the respective end-members. The model for $\text{Ca}_{1-x}\text{Co}_x\text{O}$ solid solution can be in fact considered as two-sublattice model with a Ca^{2+} – Co^{2+} mixing on cation sublattice, while the liquid is described as a mixture of phenomenological components CaO – CoO – Co or, as seen from the model parameters given in Section 4, rather as a pseudobinary mixture CaO – CoO_x with CoO_x covering the whole composition range from liquid Co –metal to CoO –oxide melt.

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