Journal of Solid State Chemistry 221 (2015) 57–65

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Oxygen potentials and phase equilibria in the system Ca–Co–O and thermodynamic properties of $Ca_3Co_2O_6$ and $Ca_3Co_4O_{9.163}$

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ARTICLE INFO

Article history:
Received 18 June 2014
Received in revised form
10 September 2014
Accepted 15 September 2014
Available online 28 September 2014

Keywords:
Oxygen non-stoichiometry
Cation non-stoichiometry
Misfit-layer calcium cobaltite
Entropy
Enthalpy of formation
Phase diagram

ABSTRACT

Oxygen potentials established by the equilibrium between three condensed phases, $CaO_{ss}+CoO_{ss}+Ca_3Co_2O_6$ and $CoO_{ss}+Ca_3Co_2O_6+Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$, are measured as a function of temperature using solid-state electrochemical cells incorporating yttria-stabilized zirconia as the electrolyte and pure oxygen as the reference electrode. Cation non-stoichiometry and oxygen non-stoichiometry in $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ are determined using different techniques under defined conditions. Decomposition temperatures and thermodynamic properties of $Ca_3Co_2O_6$ and $Ca_3Co_4O_{9.163}$ are calculated from the results. The standard entropy and enthalpy of formation of $Ca_3Co_2O_6$ at 298.15 K are evaluated. Using thermodynamic data from this study and auxiliary information from the literature, phase diagram for the ternary system Ca–Co–O is computed. Isothermal sections at representative temperatures are displayed to demonstrate the evolution of phase relations with temperature.

1. Introduction

With the emergence of thermoelectric energy conversion as an important green technology in recent times, there has been great interest in oxides with high Seebeck coefficient, good electrical and poor thermal conductivity. Misfit-layer cobaltites [1–4] have emerged as low-cost thermoelectric materials which can operate at moderately high temperatures in air. The system Ca–Co–O contains two low-dimensional ternary oxides, $Ca_3Co_2O_6$ and $Ca_3Co_4O_{9.36-\delta}$, which qualify as thermoelectric materials. Brisi and Rolando [5] first studied the system CaO–CoO–O at ~1123 K and identified two ternary oxides $Ca_3Co_2O_6$ and $Ca_9Co_{12}O_{28}$ using XRD, DTA and TG. A phase diagram for the system CaO–CoO_x in air was prepared by Woermann and Muan [6] based on microscopic and XRD examination of samples equilibrated at different temperatures. Their pseudo-binary representation showed the formation of terminal monoxide solid solutions at high temperatures and ternary oxides $Ca_3Co_2O_6$ and $Ca_3Co_4O_9$ containing Co in higher oxidation states at lower temperatures. Vidyasagar et al. [7] have reported synthesis of $Ca_2Co_2O_5$ and $CaCo_2O_4$ by thermal decomposition of carbonate solid-solution precursors in oxygen at 923 and 973 K, respectively. Subsequent research has shown that $CaCo_2O_{4+y}$, with calcium-ferrite-type structure, can be synthesized as a stable phase only at high pressure and high temperature (6 GPa, 1773 K) [8,9]. The misfit-layer compound $Ca_3Co_4O_{9.36-\delta}$ can be considered to have $Ca_2Co_2O_5$-type structure with ~25% calcium vacancies [1,10].

Structural studies [11,12] have shown that $Ca_3Co_4O_{9.36-\delta}$ is made of misfit-layer stacking of CdI_2-type CoO_2 and rock-salt (RS) type Ca_2CoO_3. The compound consists of two monoclinic subsystems CoO_2 and Ca_2CoO_3, with identical values for a, c and β. The lattice parameters are $a=0.482$, $c=1.084$ nm, $\beta=98.13°$; $b_{CoO_2}=0.282$, $b_{RS}=0.457$ nm [13]. The molar ratio between CoO_2 and Ca_2CoO_3 is approximately 26:16 or 1.62:1 implying an incommensurate structure with the formula $Ca_3Co_{3.93}O_{9.36}$. The structure can exhibit oxygen deficiency because of the formation of oxygen vacancies in the Ca_2CoO_3 block. The oxygen non-stoichiometry as a function of temperature (573 to 1223 K) and oxygen partial pressure (4 to 10^5 Pa) has been calibrated using thermogravimetry (TG) by Shimoyama et al. [14]. Jankovsky et al. [15] and Zhou et al. [16] have reported significant cationnon-stoichiometry in $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$. Jankovsky et al. [15] suggest values in the range $0.07\geq\alpha\geq-0.13$, whereas Zhou et al. [16] indicate $0.02\geq\alpha\geq0.12$. Since the misfit ratio remains virtually constant at 1.618 over the entire homogeneity range, the variable composition on both sides of the stoichiometric value is probably caused by substitutional defects, Ca for Co and Co for Ca.

$Ca_3Co_2O_6$ has hexagonal structure (space group $R\bar{3}c$) with $a=0.90793$ and $c=1.0381$ nm [17]. The structure consists of linear one-dimensional chains of Co_2O_6 along the c-axis, composed of alternating face sharing CoO_6 octahedra and CoO_6 trigonal prisms. The chains are separated by eight-coordinated Ca^{2+} ions. The face sharing characteristic in $Ca_3Co_2O_6$ is distinctly dissimilar

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http://dx.doi.org/10.1016/j.jssc.2014.09.013
0022-4596/

to edge-sharing octahedra in $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$. Cobalt ions in the octahedral environment are in the low spin state and those in the trigonal-prismatic setting are in high spin state. Hardy et al. [18] have reported specific heat measurements on $Ca_3Co_2O_6$ in the temperature range from 2 to 300 K using a two-tau relaxation method (PPMS Quantum Design). There is a specific heat peak at 26 K corresponding to a magnetic transition [16]. Below the transition temperature, $Ca_3Co_2O_6$ is ferrimagnetic, with ferromagnetic ordering within the Co–O chain [19].

Sedmiduský et al. [20] have recently used thermal analysis (DSC/DTA/TGA) in air and oxygen, XRD on quenched samples, low (2 to 300 K) and high temperature (293 to 950 K) heat capacity measurement on $Ca_3Co_4O_{9.2}$ to characterize the system Ca–Co–O and delineate the phase diagram. Much of the data in Ref. [20] overlaps with that in Ref. [15]. Identical heat capacity curves are shown for $Ca_3Co_4O_{9.2}$ in Ref. [20] and $Ca_3Co_{3.93}O_{9.37}$ in Ref. [15]. The low-temperature heat capacity exhibits a small hump at 30 K, which has been attributed to a magnetic ordering transition. Above room temperature the C_p curve reveals two distinct peaks. The sharp peak at 400 K is related to the ordering of oxygen atoms in the $[Ca_2CoO_{3-\delta}]$ block [20]. The entropy change corresponding to this transition is 5.49 J/K/mol. The second peak at 830 K, with an associated entropy change of 7.85 J/K/mol, is attributed to intermediate to high spin transition of Co^{3+} in rock-salt blocks. This transition has not been detected by other investigators. The thermal effect observed by DSC may be related to oxygen release from the sample. Sedmiduský et al. [20] combined the results of their study with other data available in the literature to assess thermodynamic properties of different phases present in the system Ca–Co–O. The misfit-layer cobaltite was modeled using the compound energy formalism. The phase diagram was computed using Factsage software. The computed diagram differs from the earlier diagram of Woermann and Muan [6] in the behavior of $Ca_3Co_2O_6$ at low temperatures. According to the recent computed diagram [20], $Ca_3Co_2O_6$ decomposes to a mixture of $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ and CaO-rich monoxide solid-solution below 1100 K in pure oxygen. Woermann and Muan [6] considered $Ca_3Co_2O_6$ to be stable at low temperatures.

These are some concerns regarding the computed diagram based on DTA/TGA inputs. First, the decomposition temperature of $Ca_3Co_2O_6$ and $Ca_3Co_4O_{9.36-\delta}$ measured in air and oxygen by DTA/TGA during heating at 10 K/min may not correspond to true equilibrium. Second, the oxygen content of the misfit phase is expected to change with temperature above 673 K during calorimetric measurement of heat capacity in air and oxygen introducing some uncertainty in the results. Third, the model used for the misfit phase has some drawbacks and many parameters of the model are not well constrained because of the limited data available. Values of the model parameters are not presented to independently verify the results or extend the model. The computed variation of oxygen non-stoichiometry with temperature and oxygen partial pressure is not in agreement with the measurements of Shimoyama et al. [14]. Fourth, the pseudo-binary representation of phase relations for the ternary system Ca–Co–O in air and oxygen is incomplete. It is essentially a projection or view of the ternary diagram from the oxygen apex. It does not reveal all the interesting features of ternary phase relations at lower oxygen partial pressures.

To rectify these shortcomings, oxygen chemical potentials associated with equilibria involving three condensed phases are measured as a function of temperature using solid-state electrochemical cells. To resolve discrepancies in the literature on the non-stoichiometry of the misfitphase, several methods were deployed. Oxygen content of samples equilibrated at well-defined temperatures and oxygen partial pressures was measured by iodometric titration and mass loss accompanying hydrogen reduction at 1200 K to CaO and Co metal. Cation non-stoichiometry was explored using XRD and EPMA. The new results refine stoichiometric limits and thermodynamic properties of $Ca_3Co_2O_6$ and $Ca_3Co_4O_{9.36-\delta}$, and permit calculation of isothermal sections of the ternary system Ca–Co–O at different temperatures revealing new features.

2. Experimental

2.1. Materials, characterization and stoichiometry

The ternary oxides $Ca_3Co_2O_6$ and $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ were synthesized by the standard solid-state reaction method staring with powders of $CaCO_3$ and Co_3O_4 of purity greater than 99.9% in the appropriate stoichiometric ratio. Two compositions of $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ with $\alpha=0$ and $\alpha=0.07$ were prepared. The powders were first mixed in a ball-mill and the homogenous mixture was gradually heated in air up to 1173 K and held at that temperature for ~72 h. The calcined powder was then pressed into pellets at 200 MPa using a steel die to ensure intimate contact between particles. The pellets were heat-treated in pure oxygen gas for ~180 h, with two intermediate regrinding and repelletization steps. Formation of ternary single phase oxide was confirmed by XRD and SEM. Cation stoichiometry of the samples was confirmed by inductively coupled plasma atomic-emission spectroscopy to an accuracy of 2%.

Samples of $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ were equilibrated in air and pure oxygen at different temperatures for 24 h and quenched in liquid nitrogen. Oxygen content was determined by iodometric titration and mass loss on hydrogen reduction to CaO and Co metal at 1200 K. A limited set of experiments were conducted on variation of oxygen non-stoichiometric parameter δ with oxygen partial pressure and temperature using a Cahn micro-balance. Oxygen partial pressure was controlled using $Ar+O_2$ gas mixtures and independently measured by an oxygen meter based on yttria-stabilized zirconia (YSZ). The oxygen content of the sample was also verified by thermogravimetry; heating the sample to 1400 K decomposed it to a mixture of CaO_{ss} and CoO_{ss}. The total oxygen content determined by this procedure was always slightly lower than that determined by iodometric titration and hydrogen reduction. The estimated accuracy in the values of δ obtained in this study is ± 0.01. The range cation non-stoichiometry of $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ was determined by EPMA on two-phase samples, $Ca_3Co_2O_6+Ca_3Co_{3.93+\alpha}O_{9.36-\delta}$ and $Ca_3Co_{3.93+\alpha}O_{9.36-\delta}+Co_3O_4$, equilibrated in oxygen at 1200 K for 48 h and rapidly cooled. The samples, contained YSZ crucibles, were sealed in evacuated quartz ampoules.

2.2. Electrochemical measurements

The reversible emfs of two solid-state cells were measured as a function of temperature. The measuring electrodes were designed using available information on phase relations in the system Ca–Co–O [6,20]. The cells can be represented as;

$$\text{Pt, } Ca_3Co_2O_6+CaO_{ss}+CoO_{ss}//(Y_2O_3)ZrO_2//O_2\text{, Pt} \quad \text{(I)}$$

$$\text{Pt, } Ca_3Co_{3.93+\alpha}O_{9.36-\delta}+Ca_3Co_2O_6+CoO_{ss}//(Y_2O_3)\ ZrO_2//O_2\text{, Pt} \quad \text{(II)}$$

The cells are written such that the right-hand reference electrode is positive. Flowing pre-purified oxygen gas at a pressure of 0.1 MPa was used as the primary reference standard for oxygen potential. YSZ tube functioned as the solid electrolyte with predominant oxygen ion conduction ($t_{ion} > 0.999$) under the experimental conditions encountered in this study. Measuring electrodes consisted of a mixture of three condensed phases, which