Phase Equilibria and Crystal Chemistry of the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ System at 885 °C in Air

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Abstract

The $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system prepared at 885 °C in air consists of two calcium cobaltate compounds, namely, the 2D thermoelectric oxide solid solution, $(\text{Ca}_{3-x}\text{Sm}_x)\text{Co}_4\text{O}_{9-z}$ ($0 \leq x \leq 0.5$) which has a misfit layered structure, and the 1D $\text{Ca}_3\text{Co}_2\text{O}_6$ which consists of chains of alternating CoO_6 trigonal prisms and CoO_6 octahedra. $\text{Ca}_3\text{Co}_2\text{O}_6$ was found to be a point compound without the substitution of Sm on the Ca site. A solid solution region of distorted perovskite, $(\text{Sm}_{1-x}\text{Ca}_x)\text{CoO}_{3-z}$ ($0 \leq x \leq 0.22$, space group *Pnma*) was established. The reported Sm_2CoO_4 phase was not observed at 885 °C, but a ternary Ca-doped oxide, $(\text{Sm}_{1+x}\text{Ca}_{1-x})\text{CoO}_{4-z}$ (*Bmab*) where $0 < x \leq 0.15$ was found to be stable at this temperature. In the peripheral binary systems, Sm was not present in the Ca site of CaO, while a small solid solution region was identified for $(\text{Sm}_{1-x}\text{Ca}_x)\text{O}_{(3-z)/2}$ ($0 \leq x \leq 0.075$). Ten solid solution tie-line regions and six three-phase regions were determined in the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system in air.

Keywords: Phase diagram of $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$; thermoelectric oxide system; tie-line phase relationships; structure for $(\text{Sm}_{1-x}\text{Ca}_x)_2\text{O}_{3-z}$, and $(\text{Sm}_{1+x}\text{Ca}_{1-x})\text{CoO}_{4-z}$

Introduction

The phenomenon of direct conversion between heat and electricity using thermoelectric (TE) materials was discovered by Seebeck and Peltier more than 150 years ago [1, 2], however, only a small number of materials have been found to have practical industrial power generation or cooling applications because of the generally low efficiencies. The efficiency and performance of TE materials is related to the dimensionless figure of merit (ZT), given by $ZT = S^2 \sigma T / \kappa$, where T is the absolute temperature, S is the Seebeck coefficient or thermopower, σ is the electrical conductivity ($\sigma = 1/\rho$, ρ is electrical resistivity), and κ is the thermal conductivity [3].

TE oxides are known to have stability at high temperatures, therefore they have been considered as possible candidates for waste heat conversion applications. Examples of these oxides include misfit layered oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ [4-13], NaCoO_x [8], $\text{Ca}_2\text{Co}_3\text{O}_6$ [9, 10], $\text{Ca}_3\text{Co}_4\text{O}_9$ [4-12], and $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_x$ [11]. Among these materials, 2D misfit layered oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ demonstrates the highest ZT [13]. Extensive efforts on improving the thermoelectric properties of this material with doping either on the Ca site or on the Co site have been reported [14-22].

As phase equilibrium diagrams provide blue prints for processing and phase relationships for designing and understanding materials properties, phase diagrams of the $\text{CaO}-\frac{1}{2}\text{R}_2\text{O}_3-\text{CoO}_z$ (R=lanthanide) systems are of interest to the thermoelectric research community. We have previously reported the phase diagram of the $\text{CaO}-\frac{1}{2}\text{La}_2\text{O}_3-\text{CoO}_z$ [23] and the $\text{CaO}-\frac{1}{2}\text{Nd}_2\text{O}_3-\text{CoO}_z$ systems [24]. In these systems, in addition to having the $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ phases, they also contain the perovskite, RCO_3 phase, which exhibit interesting thermoelectric properties. For example, the influence of ionic size of the rare-earth site on the thermoelectric properties of the RCO_3 -type perovskite cobalt oxides has been reported by Moon et al. [25]. Wang et al. [26] found that in LaCoO_3 , there is a correlation between the perovskite structural distortion and the thermoelectric response in the solid solution, $(\text{La}_{1-x}\text{Ca}_x)\text{CoO}_{3-z}$ and $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_{3-z}$. The ZT value exhibits a maximum at $x=0.1$, which is among the highest observed values in metal oxides at room temperature.

The first goal of this work is to continue establishing the phase compatibility relationships, crystal chemistry, and crystallography of selected compounds in the $\text{CaO}-\frac{1}{2}\text{R}_2\text{O}_3\text{-CoO}_z$ system at 885 °C (R=Sm in this report), particularly to obtain subsolidus phase relationships in the vicinity of the $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ compounds. The second goal of the study is to compare the phase formation and phase relationships between the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ and the $\text{CaO}-\frac{1}{2}\text{La}_2\text{O}_3\text{-CoO}_z$ systems [23].

Experimental

I. Sample Preparation

Fifty-six samples were prepared from a stoichiometric mixture of CaCO_3 , Co_3O_4 and Sm_2O_3 using high temperature solid-state techniques (Table 1). These samples were mixed, pelletized, and annealed at 750 °C for one day, and subsequently annealed at 850 °C, and 885 °C with intermediate grindings and pelletizations for another three weeks. The annealing process was repeated until no further changes were detected in the powder X-ray diffraction patterns.

Phase purity of the samples and phase relationships among the phases prepared were established using powder X-ray diffraction. Experiments were carried out using a Phillips X-ray powder diffractometer¹ (Cu K_α radiation) that was equipped with a series of Soller slits and a scintillation counter. The 2θ scanning range was from 10° to 65°, and the step interval was 0.03°. Reference diffraction patterns of compounds in the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system in the ICDD Powder Diffraction File (PDF [27]) were used for performing phase identification.

II. High resolution synchrotron Diffraction

High resolution synchrotron X-ray powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using a wavelength of 0.41380 Å. Discrete detectors covered a final angular range from 0° to 50°, with data points

¹Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedures and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology.

collected every 0.001° in 2θ at a scan speed of $0.01^\circ/\text{s}$. The instrumental optics of 11-BM incorporate two platinum-stripped mirrors and a double-crystal Si (111) monochromator, where the second crystal has an adjustable sagittal bend [28]. The diffractometer is controlled via EPICS [29]. A vertical Huber 480 goniometer positions 12 perfect Si (111) analyzers and 12 Oxford-Danfysik LaCl_3 scintillators, with a spacing of 2° in 2θ [30]. Capillary samples are mounted by a robotic arm and spun at ≈ 90 Hz. Data are normalized to incident flux and collected while continually scanning the diffractometer 2θ arm. A mixture of National Institute of Standard and Technology standard reference materials, Si (SRMTM 640c) and Al_2O_3 (SRMTM 676), is used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2θ offset, and small detector wavelength differences, before merging the data into a single set of intensities evenly spaced in 2θ .

III. Rietveld Refinements

The Rietveld refinement technique [31] with the software suite GSAS (Larson and von Dreele, 2004) [32] was used. Structural models of SmCoCo_3 and SmCaCoO_4 were used for the refinements of the structures of $\text{Sm}_{0.89}\text{Ca}_{0.11}\text{CoO}_{3-z}$ and $\text{Sm}_{1.02}\text{Ca}_{0.98}\text{CoO}_{4-z}$, respectively. The Sm and Ca atoms were constrained to occupy the same site, with a total occupancy of unity. Restraints of $1.96(2)$ Å were placed on the Co-O bonds, and $2.77(5)$ Å on the O...O cis non-bonded distances in the CoO_6 coordination sphere. The profiles were described using GSAS profile function #4 (GSAS). The LX, ptec (001), eta, and S(hkl) coefficients were refined. The background was modeled using a 6-term shifted Chebyshev polynomial.

Results and Discussion

Figure 1 gives the phase diagram of the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system that was determined at 885°C in air. The phase relationships between solid solutions and other phases are expressed as tie-line bundles. The crystal chemistry and crystallography of various phases in the binary as well as the ternary oxide systems are discussed below.

(1) CaO-CoO_x

The end member phases, Co_3O_4 and CaO , do not form solid solution, namely, Ca does not occupy the Co site in Co_3O_4 and Co does not dope in the Ca site of CaO . $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{Co}_4\text{O}_9$ are the only two binary oxide phases determined in this system [5, 14, 33].

As reported before, $\text{Ca}_3\text{Co}_4\text{O}_9$ is a misfit layered oxide that has two monoclinic subsystems with identical a , c , β , but different b values [5]. The first subsystem consists of a single CoO_2 layer, which has the CdI_2 -type structure. The second subsystem consists of triple rock-salt layers of Ca_2CoO_3 in the ab plane. The CoO_2 sheets have a strongly correlated electron system that serve as electronic transport layers, whereas the Ca_2CoO_3 layers are insulating layers. The chemical formula can be written as $[\text{Ca}_2\text{CoO}_3]\text{RS}[\text{CoO}_2]_{1.61}$, where RS is the rock salt and 1.61 expresses the incommensurable character for the b parameter of the rock salt and the CdI_2 -type structure. The $\text{Ca}_3\text{Co}_4\text{O}_9$ phase exhibits strong texture [12] and anisotropic thermoelectric properties in the ab -plane [7].

$\text{Ca}_3\text{Co}_2\text{O}_6$ belongs to the $n = 1$ member of the homologous series, $\text{A}_{n+2}\text{B}_n\text{B}'\text{O}_{3n+3}$ (where A is an alkali-earth element such as Ca, Sr, and Ba; B describes the cobalt ion inside the octahedral cage, and B' refers to the cobalt ion inside a trigonal prism). This series can be described as having 1-dimensional linear parallel $\text{Co}_2\text{O}_6^{6-}$ chains, built by successive alternating face-sharing CoO_6 trigonal prisms and CoO_6 octahedra along the hexagonal c -axis [34]. $\text{Co}_3\text{Co}_2\text{O}_6$ has a space group of $R\bar{3}c$, with $a = 9.0793(7)$ Å, and $c = 10.381(1)$ Å [35], Fig. 2). The linear $\text{Co}_2\text{O}_6^{6-}$ chains consist of one CoO_6 octahedron alternating with one CoO_6 trigonal prism. Each $\text{Co}_2\text{O}_6^{6-}$ chain is surrounded by six other chains which form a hexagonal arrangement. The members in $\text{A}_{n+2}\text{Co}_n\text{Co}'\text{O}_{3n+3}$ can also be considered as ordered intergrowth between the $n = \infty$ (ACoO_3) and $n = 1$ ($\text{A}_3\text{Co}_2\text{O}_6$) end members [8, 36].

(ii) $\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CaO}$

At 885 °C, no intermediate phases form in this system other than the $(\text{Sm}_{1-x}\text{Ca}_x)\text{O}_{(3-z/2)}$ ($0 \leq x \leq 0.075$) solid solution. The $(\text{Sm}_{1-x}\text{Ca}_x)_2\text{O}_{3-z}$ phase crystallizes in a monoclinic structure [37]. We found the solubility of Sm_2O_3 in CaO to be negligible at 885 °C.

(iii) $\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_x$

The only phase found in the $\text{Sm}_2\text{O}_3\text{-CoO}_x$ system was the SmCoO_3 phase having the perovskite structure with space group $Pnma$, $a=5.350\text{\AA}$, $b=7.496\text{\AA}$, and $c=5.283\text{\AA}$ (PDF: 4-008-0074) [27, 38]. The Sm_2CoO_4 phase could not be prepared at $885\text{ }^\circ\text{C}$. However, it was reported to exist as single crystals when Sm_2O_3 and CoO were heated above 2273 K by CO_2 -laser techniques using zirconia crucible under the argon atmosphere. It could also be prepared at higher temperature of $1200\text{ }^\circ\text{C}$ [39] and is therefore absent in the current phase diagram. Sm_2CoO_4 is the $n=1$ member of the Ruddlesden-Popper family of compounds, $A_{n-1}A'_2B_nO_{3n+1}$, where A , A' and B are cations, and 'n' is the number of the layers of octahedra in the perovskite stack. The structure of Sm_2CoO_4 was determined from single crystal to be orthorhombic $Fmm2$ (No. 42) with $a=5.363\text{\AA}$, $b=11.869\text{\AA}$, and $c=5.312\text{\AA}$ (PDF: 4-13-8634 [27, 40]).

(iv) $\text{CaO-}\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_x$ system

Three ternary solid solutions were found in this system. The first solid solution is the Sm-doped $\text{Ca}_3\text{Co}_4\text{O}_9$ phase $(\text{Ca}_{3-x}\text{Sm}_x)\text{Co}_4\text{O}_{9-z}$ ($0 \leq x \leq 0.5$). The second solid solution is the Ca-doped SmCoO_3 phase, $(\text{Sm}_{1-x}\text{Ca}_x)\text{CoO}_{3-z}$ ($0 \leq x \leq 0.22$). Although a small homogeneity range of the $(\text{Ca}_{3-x}\text{Sm}_x)\text{Co}_4\text{O}_9$ phase was found, solid solution by substituting Sm at the Ca site in $\text{Ca}_3\text{Co}_2\text{O}_6$ does not form at $885\text{ }^\circ\text{C}$. It was reported earlier that in the $\text{CaO-}\frac{1}{2}\text{R}_2\text{O}_3\text{-CoO}_z$ ($\text{R}=\text{La}$ and Nd) systems, no solid solution formation was found with La or Nd doping in the Ca site of the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase as well [23, 24].

Another solid solution found in the $\text{CaO-}\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system is $(\text{Sm}_{1-x}\text{Ca}_x)_2\text{CoO}_4$. Thorogood et. al. (2011) [41] reported the structure, crystal chemistry and magnetism of a series of lanthanide (Ln)-rich calcium cobaltates: $\text{Ln}_{2-x}\text{Ca}_x\text{CoO}_{4+\delta}$. They found that when the size of Ln is large ($\text{Ln}=\text{La}^{3+}$, Pr^{3+} - Sm^{3+}) or for compositions containing the smaller lanthanide ions ($<\text{Gd}^{3+}$) and Y^{3+} [42], the structure is tetragonal $I4/mmm$ at room temperature, while $\text{Ln}=\text{Eu}$ to Gd , the structure is orthorhombic $Bmab$. On the other hand, Taguchi et al. [43] reported that the Ca-rich solid solution, $(\text{Ca}_{1-x}\text{Sm}_{1+x})\text{CoO}_{4-\delta}$ (up to $(\text{Ca}_{1.15}\text{Sm}_{0.85})\text{CoO}_4$) was obtained instead when using chemical solution method at about $2000\text{ }^\circ\text{C}$ and under Ar atmosphere. However, Ca-rich single phase solid solution region of $(\text{Ca}_{1+x}\text{Sm}_{1-x})\text{CoO}_{4-\delta}$ was confirmed to be absent in this study. We found that the solid solution region is Sm-rich $(\text{Ca}_{1-x}\text{Sm}_{1+x}\text{Co})\text{O}_{4-z}$, with $0 < x \leq 0.15$.

This phase has the distorted K_2NiF_4 -type structure [43]), which is a member of the Ruddlesden-Popper family of compounds.

The results of structural study of $(Ca_{1-x}Sm_{1+x}Co)O_{4-z}$ and $(Sm_{1-x}Ca_x)CoO_{3-z}$ using the synchrotron X-ray diffraction at the APS are discussed below and the results are listed in Tables 2 to 7, and Figs 3-8.

$(Sm_{1-x}Ca_x)CoO_{3-z}$ (x=0.11)

The observed (crosses), calculated (solid line), and difference (bottom) XRD patterns for $(Sm_{1-x}Ca_x)CoO_{3-z}$, as determined by the Rietveld analysis technique, are shown in Fig. 3. The difference pattern is plotted at the same scale as the other patterns up to $18^\circ 2\theta$. At higher angles, the scale has been magnified five times. The row of tick marks refers to the calculated peak positions. Results of X-ray Rietveld refinements of $(Sm_{0.89}Ca_{0.11})CoO_{3-z}$ are shown in Table 2. Table 3 gives the lattice parameters for this compound. Tables 4 and 5 provide atomic coordinates and selected bond distances, respectively. $(Sm_{0.89}Ca_{0.11})CoO_{3-z}$ has the orthorhombic *Pnma* perovskite structure. The lattice parameters of the compound was found to be $a=5.350819(13)\text{\AA}$, $b=7.49989(2)\text{\AA}$, $c=5.290989(12)\text{\AA}$, and $V=212.3303(10)\text{\AA}^3$.

The Goldschmidt geometrical tolerance factor (t) is often used to quantify the degree of distortion of a perovskite compound. The tolerance factor t is written as $t=\langle r_A+r_O \rangle / \sqrt{2} \langle r_B+r_O \rangle$ [44], where $\langle r_A+r_O \rangle$ represents the average cation-oxygen distance on the A site and $\langle r_B+r_O \rangle$ is the average cation-oxygen distance on the B site of the perovskite structure, with $t=1$ being the ideal cubic perovskite situation. As t approaches 1, the structure is expected to become less distorted; with $t<1$ the distortion is accommodated by the cooperative rotation of the BO_6 octahedra, resulting in a lower symmetry. In $(Sm_{1-x}Ca_x)CoO_{3-z}$, the coordination number (c.n.) is 10 for the Ca^{2+}/Sm^{3+} cations, and 6 for the Co^{3+} ion. As the ionic radii for Sm^{3+} with c.n.=10 is not available according to Shannon [42], the ionic radii of the Ca^{2+} , and Sm^{3+} , ions with a c.n. of 9 (1.18, and 1.132 $\text{\AA}$ respectively) were used for the 't' value computation instead [42]. In $(Sm_{1-x}Ca_x)CoO_{3-z}$, doping on the Sm site with a larger cation Ca^{2+} [42] increases the effective mean ionic radius of the A site, thus increasing the 't' value slightly as compare to that in

SmCoO₃. The 't' values for (Sm_{1-x}Ca_x)CoO_{3-z} with x=0 and 0.15 are calculated to be 0.933 and 0.936, respectively.

In orthorhombic (Sm_{1-x}Ca_x)CoO_{3-z}, there are two distinct Co-O-Co angles (Co3-O4-Co3 and Co3-O5-Co3) that are between different octahedral units. While the Co3-O4-Co3 angle (153.07(12)°) is a measure for the deviation from ideal value of 180° along the *b*-axis, the Co3-O5-Co3 bending (153.39(9)°) is related to the rotation of the CoO₆ octahedra with respect to the *ac* plane (Figs. 4 and 5). In Table 5, one notes that the Co3 sites also have distorted octahedral environment as evidenced from the slightly different Co-O distances.

Structure of (Ca_{1-x}Sm_{1+x})CoO_{4-z} (x=0.02)

In Fig. 6, results of Rietveld refinements, including the observed (crosses), calculated (solid line), and difference neutron diffraction patterns (bottom) for (Sm_{1.02}Ca_{0.98})CoO_{4-z}, are shown. The difference pattern is plotted at the same scale as the other patterns up to 18° 2θ. At higher angles, the scale has been magnified five times. The row of tick marks refers to the calculated peak positions. The atomic coordinates and displacement parameters are given in Table 6 and selected bond distances are listed in Table 7.

The structure of CaSmCoO₄ has been controversial. It has been reported to be K₂NiF₄-type tetragonal *I4/mmm* [27, 43] (PDF 00-60-811) and orthorhombic *Cmca* (PDF 4-14-8171) [27]. Furthermore, according to Payom and Daire [46], CaLnCoO₄ (Ln = Pr and Nd) has a tetragonal K₂NiF₄- structure and retains this structure at high temperatures, whereas CaLnCoO₄ (Ln = Sm and Gd) has a monoclinic K₂NiF₄-type structure at room temperature. The phase transition to the tetragonal K₂NiF₄-type structure occurs at 423 K. In the present study, we found that the structure agrees with that reported by Taguchi et al. [45]. (Sm_{1.02}Ca_{0.98})CoO_{4-z} is isostructural with (Sm_{1.1}Ca_{0.9})CoO_{4-z} (04-18-7120; orthorhombic *Abam* [22], [47]). In the (Sm_{1+x}Ca_{1-x})CoO₄ solid solution, the valence of Co ion can vary between 3+ and 2+ by changing the Ca/Sm ratio. Therefore, it is expected that Co³⁺ and Co²⁺ ions coexist in the (Sm_{1.02}Ca_{0.98})CoO_{4-z} compound.

In the (Sm_{1+x}Ca_{1-x})CoO₄ structure, it is confirmed that two-dimensional perovskite layers were formed as a result of corner-sharing CoO₆ octahedra. These layers are interleaved with the

rocksalt-like Sm/Ca-O layers in the *c*-direction (Figs. 7 and 8). Sm³⁺ and Ca²⁺ occupy the same crystallographic site. In (Sm_{1.02}Ca_{0.98})CoO_{4-z}, the coordination number (c.n.) is 9 for the Ca²⁺/Sm³⁺ cations, and 6 for the Co³⁺ ion. According to Shannon, the ionic radii of the Ca²⁺, and Sm³⁺, ions with a coordination of 9 are 1.18 Å and 1.132 Å, respectively [42]. Therefore the cell volume of CaSmCoO₄ is slightly greater than that of the (Sm_{1.02}Ca_{0.98})CoO_{4-z} phase.

Table 3 gives the (Ca, Sm)–O distances, the Co–O distances, the O–Co–O angles, and the Co–O–Co angle of Sm_{1+x}Ca_{1-x}CoO₄. The A-site cation (Ca or Sm ion) coordinates with four O4 ions and six O5 ions. The B-site cation (Co ion) coordinates with four O4 ions and two O5 ions [48]. The Co–O–Co angle (Co3–O4–Co3) that is between different octahedral units was found to be 3.3(5)° deviated from an ideal value of 180° along the *b*-axis (Figs. 3 and 4). One notes that the Co3 sites also have distorted octahedral environment as evidenced from the slightly different Co–O distances (The equatorial Co–O4 distance is 1.8605(2) Å, whereas the axial Co–O5 distance is 1.987(2) Å). While axial O(4)–Co3–O(4) and the O(5)–Co–O(5) angles are linear, the remaining O(4)–Co3–O(4) and O4–Co3–O5 angles are slightly distorted (89.945(14)° and 89.0(3)° instead of 90.0°).

According to Taguchi et al. [45] CaSmCoO_{4-z} is a p-type semiconductor and shows paramagnetic behavior above 5 K. The 1/χ–T curve of CaSmCoO_{4-z} was found to deviate from the Curie–Weiss law in the temperature range of (5 ≤ T ≤ 300) K. From the values of the observed effective magnetic moment (μ_{eff}) of CaSmCoO₄, the spin state of the Co³⁺ ion was considered to be low.

(v) Comparison of phase relationships in the CaO- 1/2La₂O₃-CoO_x and CaO- 1/2Sm₂O₃-CoO_x systems

Figure 9 depicts the phase diagrams of the CaO-1/2La₂O₃-CoO_z system prepared at 885 °C in air [23]. While a comparison of the La- and Sm-containing systems reveals substantial differences in terms of phase formation and phase relationships, there are similarities in these systems as well. In both systems, Ca₃Co₂O₆ and CaO are stoichiometric compounds. Solid solution formation was observed in phases (Ca,R)₃Co₄O₉, (R_{1-x}Ca_x)CoO_{3-z}, and (R_{1-x}Ca_x)₂O_{3-z} (R=La

and Sm). The $(R_{1+x}Ca_{1-x})CoO_{4-z}$ phase was not found in the La-system, which alter the appearance of the diagrams substantially. While both systems contain the perovskite $RCoO_3$ phase, the structures of $LaCoO_3$ and $SmCoO_3$ are different from each other. The $LaCoO_3$ phase is rhombohedral with a space group $R\bar{3}c$ [24], but $SmCoO_3$ is orthorhombic with a space group $Pnma$ [35]. The difference in ionic size of the lanthanide ions ($r_{La}^{3+} > r_{Ca}^{2+} > r_{Sm}^{3+}$) [42] governs the extent of solid solutions of $(R_{1-x}Ca_x)CoO_{3-z}$, $(R_{1-x}Ca_x)_2O_{3-z}$, and $(R_{1+x}Ca_{1-x})CoO_{4-z}$.

Because of different phase formation and different range of solid solutions in the Sm- and the La-systems at 885 °C, the tie-line relationships are substantially different. In the R=La system, there are four three-phase regions, and a total of four two-phase tie-line bundles [23]. These three-phase regions are: $CoO_z-(La_{0.8}Ca_{0.2})CoO_{3-z}-(Ca_{0.93}La_{0.07})_3Co_4O_9$; $(La_{0.8}Ca_{0.2})CoO_{3-z}-(Ca_{0.93}La_{0.07})_3Co_4O_9-Ca_3Co_2O_6$; $(La_{0.8}Ca_{0.2})CoO_{3-z}-Ca_3Co_2O_6-CaO$, and $(La_{0.8}Ca_{0.2})CoO_{3-z}-(La_{0.92}Ca_{0.08})_2O_{3-z}-CaO$. The tie-line bundles extended from CoO_z to $(La,Ca)CoO_{3-z}$, from $(La,Ca)CoO_{3-z}$ to $(La,Ca)_2O_{3-z}$, from CoO_z to $(Ca,La)_3Co_4O_9$, and from $(Ca,La)_3Co_4O_9$ to $Ca_3Co_2O_6$.

In the case of the R=Sm system, there are a total of six three-phase regions and seven tie-line bundles. These tie-line bundles are defined by $CoO_z-(Sm_{1-x}Ca_x)CoO_{3-z}$; $CoO_z-(Ca,Sm)_3Co_4O_9$; $(Ca_{1-x}Sm_{1+x}Co)O_{4-z}-(Sm_{1-x}Ca_x)CoO_{3-z}$; $(Ca,Sm)_3Co_4O_9-Ca_3Co_2O_6$; $(Sm_{1-x}Ca_x)_2O_{3-z}-(SmNd_{1-x}Ca_x)CoO_{3-z}$; $(Sm_{1-x}Ca_x)_2O_{3-z}-(Ca_{1-x}Sm_{1+x}Co)O_{4-z}$; $Ca_3Co_2O_6-(Ca_{1-x}Sm_{1+x}Co)O_{4-z}$; and $CaO-(Ca_{1-x}Sm_{1+x}Co)O_{4-z}$. The six three-phase regions are defined by $CoO_z-(Sm_{0.75}Ca_{0.25})CoO_{3-z}-(Ca_{2.5}Sm_{0.5})Co_4O_{9-z}$; $(Sm_{0.75}Ca_{0.25})CoO_{3-z}-(Ca_{2.5}Sm_{0.5})Co_4O_{9-z}-Ca_3Co_2O_6$; $(Sm_{0.75}Ca_{0.25})CoO_{3-z}$, $Ca_3Co_2O_6-(Ca_{1-x}Sm_{1+x}Co)O_{4-z}$; $(Ca_{1-x}Sm_{1+x}Co)O_{4-z}-SmCoO_3-\frac{1}{2}[(Sm_{0.925}Ca_{0.075})_2O_{3-z}]$; $(Ca_{1-x}Sm_{1+x}Co)O_{4-z}-\frac{1}{2}[(Sm_{0.925}Ca_{0.075})_2O_{3-z}]-CaO$; and $(Ca_{1-x}Sm_{1+x}Co)O_{4-z}-CaO-Ca_3Co_2O_6$.

Summary

The phase diagram of the $CaO-\frac{1}{2}Sm_2O_3-CoO_z$ system was determined at 885 °C in air. This diagram offers detailed compatibility relationships in the ternary oxide system that are essential for processing and for the understanding of material properties. The diagram of the $CaO-$

$\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_z$ system is distinctively different from that determined for the $\text{CaO-}\frac{1}{2}\text{La}_2\text{O}_3\text{-CoO}_z$ system. The homogeneity range of the two low-dimensional phases, namely, $(\text{Ca}, \text{Sm})_3\text{Co}_4\text{O}_9$ (misfit layered structure), $(\text{Sm}, \text{Ca})_{n+2}\text{Co}_n\text{Co}'\text{O}_{3n+3}$ (with one dimensional cobalt oxide chains), and the distorted perovskite-related phases, $(\text{Sm}, \text{Ca})\text{CoO}_3$ and $(\text{Sm}_{1+x}\text{Ca}_{1-x})\text{CoO}_{4-z}$ are established. As the best cobaltate materials for thermoelectric applications, at present, are still the $\text{Ca}_3\text{Co}_4\text{O}_9$ type of compounds that feature misfit layered structure, we plan to continue to determine the phase diagrams of the $\text{CaO- R}_2\text{O}_3\text{-CoO}_z$ systems, with $\text{R} = \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}$, and Yb , in the near future.

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Table 1. Samples prepared for the phase equilibria study of the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_x$ system at 885 °C in air. In this table, Ca =CaO; Sm= $\frac{1}{2}\text{Sm}_2\text{O}_3$; Co= $\frac{1}{3}\text{Co}_3\text{O}_4$

Sample #	Ca	Sm	Co
#1	--	66.667	33.333
#2	6.667	60	33.333
#3	16.667	50	33.333
#4	23.33	43.33	33.33
#5	26.67	40.0	33.33
#6	28.33	38.33	33.33
#7	30.0	36.667	33.333
#8	31.667	35.0	33.333
#9	33.333	33.333	33.333
#10	35.0	31.667	33.333
#11	32.0	34.667	33.333
#12	32.50	34.17	33.33
#13	36.667	30.0	33.333
#14	38.33	28.33	33.333
#15	---	50	50
#16	5	45	50
#17	7.5	42.5	50
#18	10	40	50
#19	12.5	37.5	50
#20	15	35	50
#21	41.43	1.43	57.14
#22	40	2.86	57.14
#23	38.57	4.29	57.14
#24	37.14	5.72	57.14
#25	35.72	7.14	57.14
#26	34.29	8.57	57.14
#27	32.86	10.00	57.14
#28	31.43	11.43	57.14
#29	30	12.86	57.14
#30	59	1	40
#31	58	2	40
#32	56	4	40
#33	54	6	40
#34	5	95	0
#35	4	96	0
#36	7.5	92.5	0
#37	10	90	0
#38	15	85	0
#39	17.5	82.5	0
#40	25	75	0
#41	30	70	0

#42	35	65	0
#43	99.0	1.0	0
#44	98.0	2.0	0
#45	95	5	0
#46	35	25	40
#47	65	10	25
#48	45	40	15
#49	5	75	20
#50	20	15	65
#51	30	20	50
#52	2	38	60
#53	20	37.5	42.5
#54	55	21	24
#55	20	60	20
#56	39	31	30

Table 2. Refinement Residuals for (Sm_{0.89}Ca_{0.11})CoO_{3-z} and (Sm_{1.02}Ca_{0.98})CoO_{4-z}
(synchrotron radiation, $\lambda=0.41380$ Å)

	(Sm _{0.89} Ca _{0.11})CoO _{3-z}	(Sm _{1.02} Ca _{0.98})CoO _{4-z}
Rwp	0.1086	0.1157
Rp	0.0758	0.0909
χ^2	2.082	1.96
R(F ²)	0.0477	0.0489
Profile X <i>ptec</i> (001) Size, Å	0.828(7) 12,000	0.145 (15) 0.52(2)
<i>S</i> (400)	0.363(5)	0.200(3)
<i>S</i> (040)	0.021(1)	0.360(3)
<i>S</i> (004)	0.185(6)	0.0491(6)
<i>S</i> (220)	0.032(2)	-0.043(6)
<i>S</i> (202)	-0.029(4)	0.081(2)
<i>S</i> (022)	0.036(2)	-0.046(1)

Table 3. Refined Lattice Parameters for $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$ (*Pnma*), and $(\text{Sm}_{1.02}\text{Ca}_{0.98})\text{CoO}_4$ (*Bmab*). The values in parentheses represent standard deviations.

x	$(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$	$(\text{Sm}_{1.02}\text{Ca}_{0.98})\text{CoO}_{4-z}$
$a, \text{\AA}$	5.350819(13)	5.25984(4)
$b, \text{\AA}$	7.49989(2)	5.26043(2)
$c, \text{\AA}$	5.290989(12)	11.87205(5)
$V, \text{\AA}^3$	212.3303(10)	328.488(2)

Table 4. Atomic coordinates and displacement parameters for $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$ (*Pnma*). The displacement factors (U_{iso}) have been multiplied by 100. The values in parentheses represent standard deviations.

Atoms	x	y	z	Uiso	Occ.
Sm1/Ca2	0.04549(3)	$\frac{1}{4}$	-0.00897(5)	0.380(4)	0.892(2)/0.108(2)
Co3	$\frac{1}{2}$	0	0	0.241(10)	1.0
O4	0.4817(4)	$\frac{1}{4}$	0.0828(4)	0.43(3)	1.0
O5	0.2908(3)	0.4574(2)	- 0.2916(3)	0.43(3)	1.0

Table 5. Selected bond distances (Å) for $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$.
The values in parentheses represent standard deviations.

Atom-Aom		Distance (Å)
Sm1/Ca2-O4		3.0553(2)
	-O4	2.384(2)
	-O4	3.055(2)
	-O4	2.280(2)
	-O5 x2	2.526(2)
	-O5 x2	2.628(2)
	-O5 x2	2.3220(15)
Co3	-O4 x2	1.9280(5)
	-O5 x2	1.9337(11)
	-O5 x2	1.9325(11)

Table 6. Refined atomic coordinates and displacement parameters for $(\text{Sm}_{1.02}\text{Ca}_{0.98})\text{CoO}_{4-z}$, space group *Bmab*, $a=5.25984(4)$ Å, $b=5.26043(2)$ Å, and $c=11.87205(5)$ Å, $Z=4$. The displacement factors (U_{iso}) have been multiplied by 100. The values in parentheses represent standard deviations.

	frac	x	y	z	U_{iso}
Sm1/Ca2	.512(1)/.488(1)	0	0.0035(2)	0.36033(2)	0.453(6)
Co3	1.0	0	0	0	0.124(13)
O4	1.0	$\frac{1}{4}$	$\frac{1}{4}$	0.0045(7)	1.26(3)
O5	1.0	0	-0.0060(14)	0.16735(15)	1.26(3)

Table 7a. Selected bond distances (Å) in (Sm_{1.02}Ca_{0.98})CoO_{4-z}, space group *Bmab*, $a=5.25984(4)$ Å, $b=5.26043(2)$ Å, and $c=11.87205(5)$ Å, $Z=4$. The values in parentheses represent standard deviations.

Atom-Atom		Bond distance
Sm1/Ca2-O4	x2	2.518(5)
	-O4 x2	2.466(5)
	-O5 x2	2.6504(2)
	-O5	2.292(2)
	-O5	2.700(7)
	-O5	2.601(7)
Co3	-O4 x4	1.8605(2)
	-O5 x2	1.987(2)

Table 7b. Selected bond angles (°) in $\text{Sm}_{1.02}\text{Ca}_{0.98}\text{CoO}_{4-z}$ (*Bmab*, $a=5.25984(4)$ Å, $b=5.26043(2)$ Å, and $c=11.87205(5)$ Å, $Z=4$). The values in parentheses represent standard deviations.

Atom-Atom-Atom	Angle (°)
Co3-O4-Co3	176.7(5)
O4-Co3-O4	180.0 89.94 (1)
O5-Co3-O5	180.0
O4-Co3-O5	89.0(3) 91.0(3)

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FIGURE LEGENDS

Fig. 1. Phase diagram of the $\text{CaO}-\frac{1}{2}\text{Sm}_2\text{O}_3\text{-CoO}_x$ system at 885 °C in air, showing the limits of various solid solutions, and the tie-line relationships of various phases.

Fig. 2. Crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ ($n = 1$ member in $\text{Ca}_{n+2}\text{Co}_n\text{CoO}_{3n+3}$), showing the feature of linear chains of successive alternations of CoO_6 octahedron with CoO_6 prism.

Fig. 3. The observed (crosses), calculated (solid line), and difference XRD patterns (bottom) for $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$, as determined by the Rietveld analysis technique.

Fig. 4. Structure of $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$ (*Pnma*) view along *b*-axis., showing distorted corner-sharing octahedra. Small pink balls in the middle of the CoO_6 octahedra represent ‘Co3’.

Fig. 5. Structure of $(\text{Sm}_{0.89}\text{Ca}_{0.11})\text{CoO}_{3-z}$ (*Pnma*) view along *a*-axis. The Co3-O4-Co3 and Co3-O5-Co3 angles were determined to be $153.67(12)^\circ$ and $153.99(9)^\circ$ for $x=0.15$, respectively.

Fig. 6. The observed (crosses), calculated (solid line), and difference XRD patterns (bottom) for $(\text{Sm}_{1.01}\text{Ca}_{0.09})\text{CoO}_{4-z}$, as determined by the Rietveld analysis technique.

Fig. 7. Structure of $\text{Sm}_{1.02}\text{Ca}_{0.98}\text{CoO}_4$ (*Bmab*) view along the diagonal of the *ab*-axis. The structure is of the K_2NiF_4 type.

Fig. 8. Structure of $\text{Sm}_{1.02}\text{Ca}_{0.98}\text{CoO}_4$ (*Bmab*) view along the diagonal of the *b*-axis. The structure is of the K_2NiF_4 type.

Fig. 9. Phase diagram of the $\text{CaO}-\frac{1}{2}\text{La}_2\text{O}_3\text{-CoO}_x$ system at 885 °C in air [23].

FIGURES

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