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Crystal chemistry and phase equilibria of the CaO-1/2Dy_2O_3-CoO_z system at 885 $^\circ\text{C}$ in air



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ARTICLEINFO	A B S T R A C T	
A R T I C L E I N F O <i>Keywords:</i> Phase diagram of CaO-½Dy ₂ O ₃ -CoO _z at 885 °C in air Thermoelectric oxide (Ca _{3-x} Dy _x)Co ₄ O _{9-z} Phase relationships	The CaO- $\frac{1}{2}$ Dy ₂ O ₃ -CoO _z system prepared at 885 °C in air consists of two calcium cobaltate compounds. The 2D thermoelectric oxide, $(Ca_{3,x}Dy_x)Co_4O_{9,z}$ ($0 \le x \le 0.6$) has a misfit layered structure, and the 1D Ca ₃ Co ₂ O ₆ consists of chains of alternating CoO ₆ trigonal prisms and CoO ₆ octahedra. Ca ₃ Co ₂ O ₆ was found to be a stoichiometric compound without the substitution of Dy on the Ca site. No solid solution of the distorted perovskite, $(Dy_{1,x}Ca_x)CoO_{3,z}$ was established at this temperature. In the CaO-Dy ₂ O ₃ system, while a small solid solution region was identified for $(Dy_{1,x}Ca_x)O_{(3,z)/2}$ ($0 \le x \le 0.075$), Dy was not present in the Ca site of CaO. Neither the reported Dy_2CoO_4 phase in the Dy_2O -CoO _z system nor the Ca-doped $(Dy_{1+x}Ca_{1,x})CoO_{4-z}$ phase was present at 885 °C. Three solid solution tie-line regions and four three-phase regions were determined in the CaO- $\frac{1}{2}Dy_2O_3$ -CoO _z system. A comparison of the phase diagrams in the CaO- $\frac{1}{2}R_2O_3$ -CoO _z (R = La, Gd and Dy) systems is presented.	

1. Introduction

Despite world-wide intense research of thermoelectric (TE) materials, 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 [1]. However, optimizing these properties is a formidable task because of the interdependence of these properties.

TE oxides (examples include misfit layered oxide Ca₃Co₄O₉ [2–13], NaCoO_x [6], Ca₂Co₃O₆ [7,8], Ca₃Co₄O₉ [2–10], Bi₂Sr₂Co₂O_x [9], and the natural superlattices (Bi,A)Cu₂Se₂O (A = Pb, Ba, Sr, and Ca) [10,11]) are known to be stable at high temperatures and have been considered as possible candidates for waste heat conversion applications. Among these materials, the 2D misfit layered oxide Ca₃Co₄O₉ is among the oxides with the highest *ZT* [12,13]. Extensive efforts on improving the thermoelectric properties of this material with dopants either on the Ca site or on the Co site have been carried out [14–22].

As phase equilibrium diagrams which provide blue prints for processing and understanding phase relationships are important for designing and understanding materials properties, phase diagrams of the

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https://doi.org/10.1016/j.solidstatesciences.2018.12.010 Received 27 November 2018; Accepted 12 December 2018 Available online 13 December 2018 1293-2558/ Published by Elsevier Masson SAS. CaO- $\frac{1}{2}R_2O_3$ -CoO_z (R = lanthanide) systems are of interest to the thermoelectric research community. We have previously reported the phase diagrams for the CaO- $\frac{1}{2}R_2O_3$ -CoO_z systems with R = La [23], Nd [24], Sm [25], Eu [26], Gd [27], and for the CaO-SrO-CoO_z [14], and CaO-ZnO-CoO_z systems [28]. In the CaO- $\frac{1}{2}R_2O_3$ -CoO_z systems, in addition to having the Ca₃Co₄O₉ and Ca₃Co₂O₆ phases, they also contain the perovskite RCoO₃ phase, which exhibit interesting thermoelectric properties. For example, the influence of ionic size of the rare-earth site on the thermoelectric properties of the RCoO₃-type perovskite cobalt oxides has been reported by Moon et al. [29]. Wang et al. [30] found that in LaCoO₃, there is a correlation between the perovskite structural distortion and the thermoelectric response in the solid solutions (La₁. xCa_x)CoO_{3-z} and (La_{1-x}Sr_x)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 at the time.

The first goal of this work is to continue establishing the phase compatibility relationships, crystal chemistry, and crystallography of selected compounds in the CaO- $\frac{1}{2}R_2O_3$ -CoO_z system at 885 °C (R = Dy in this report), particularly to obtain subsolidus phase relationships in the vicinity of the Ca₃Co₄O₉ and Ca₃Co₂O₆ compounds. The second goal is to study the possible formation of solid solutions of (Dy₁ _xCa_x)CoO_{3-z} and (Ca_{1-x}Dy_x)₂Co₃O₆ using X-ray diffraction. The third goal of the study is to compare the phase formation and phase relationships between the CaO- $\frac{1}{2}La_2O_3$ -CoO_z [23], CaO- $\frac{1}{2}Gd_2O_3$ -CoO_z

[27], and the CaO- $\frac{1}{2}$ Dy₂O₃-CoO_z systems. The fourth goal is to prepare X-ray reference patterns [31,32] of selected members of the (Dy₁, xCa_x)CoO_{3-z} and (Ca_{1-x}Dy_x)₂Co₃O₆ series, if they are confirmed to be stable phases at 885 °C. These reference patterns will be included in the ICDD Powder Diffraction File (PDF [33]).

2. Experimental

2.1. Sample preparation

Forty-eight samples were prepared from a stoichiometric mixture of CaCO₃, Co₃O₄ and Dy₂O₃ 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.

2.2. X-ray diffraction

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 2 θ scanning range was from 10° to 65°, and the step interval was 0.03°. Reference diffraction patterns of compounds in the CaO-½Dy₂O₃-CoO_z system in the PDF [33] were used for performing phase identification.

2.3. Rietveld refinements

For structure analysis, compositions of $(Dy_{0.9}Ca_{0.1})CoO_3$ and $(Dy_{0.8}Ca_{0.2})CoO_3$, and $(Ca_{2.9}Dy_{0.1})Co_2O_6$ were mounted as ethanol slurries on a zero-background cell. The powder patterns were measured on a PANalytical Empyrean diffractometer equipped with an incident-beam focusing mirror and an X'Celerator detector. The patterns $(1^{\circ}-100^{\circ}\ 20\ range,\ 0.008356^{\circ}\ per\ step,\ 4\ s/step,\ 1/4\ ^{\circ}\ divergence\ slit,\ 0.02\ radian\ Soller\ slits)$ were measured from a rotated 0.3 mm capillaries using Mo K α radiation. The Rietveld refinement technique [34] with software suite GSAS [35] was employed along with DyCoO₃ and Ca₃Co₂O₆ as the initial models. In both cases, the Dy and Ca atoms were constrained to occupy the same site, with a total occupancy of unity.

3. Results and discussion

Fig. 1 gives the phase diagram of the CaO- $\frac{1}{2}$ Dy₂O₃-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.

3.1. Binary oxide systems

CaO-CoO_z

The end member phases, CoO_z and CaO, do not form solid solution, namely, Ca does not occupy the Co site in CoO_z and Co does not dope in the Ca site of CaO. $Ca_3Co_2O_6$ and $Ca_3Co_4O_9$ are the only two binary oxide phases found in this system [3,14,36]. $Ca_3Co_4O_9$ is a misfit

Table 1

Forty-eight samples (mole fraction, %) prepared for the phase equilibria study of the CaO- $1/2Dy_2O_3$ -CoO_z system at 885 °C in air. In this table, Ca = CaO; Dy = $1/2Dy_2O_3$; Co = 1/3 Co₃O₄.

	Ca	Dy	Со
#1	_	66.667	33.333
#2	16.667	50	33.333
#3	33.333	33.333	33.333
#4	30.0	36.667	33.333
#5	35.0	31.667	33.333
#6	32.50	34.17	33.33
#7	31.667	35.0	33.333
#8	36.667	30.0	33.333
#9	28.33	38.33	33.33
#10	38.33	28.33	33.333
#11	26.67	40.0	33.33
#12	23.33	43.33	33.33
#13	5	45	50
#14	10	40	50
#15	7.5	42.5	50
#16	15	35	50
#17	12.5	37.5	50
#18	25.0	25.0	50
#19	20.0	30.0	50
#20	41.43	1.43	57.14
#21	40	2.86	57.14
#22	38.57	4.29	57.14
#23	37.14	5.72	57.14
#24	35.72	7.14	57.14
#25	34.29	8.57	57.14
#26	32.86	10.00	57.14
#27	58	2	40
#28	56	4	40
#29	59	1	40
#30	35	25	40
#31	65	10	25
#32	45	40	15
#33	5	75	20
#34	20	15	65
#35	30	20	50
#36	2	38	60
#37	5	95	0
#38	4	96	0
#39	7.5	92.5	0
#40	10	90	0
#41	12.5	87.5	0
#42	98.0	2.0	0
#43	99.0	1.0	0
#44	95	5	0
#45	20	37.5	42.5
#46	55	21.5	23.5
#47	20	60	20
#48	39	31	30

layered oxide that has two monoclinic subsystems with identical a, c, β , but different b values [3,37] (Fig. 2). The first subsystem consists of a single CoO₂ layer, which has the CdI₂-type structure. The second subsystem consists of triple rock-salt layers of Ca₂CoO₃ in the *ab* plane. There is an incommensurate spatial modulation along one of the two inlayer crystal axes, that is, the *b*-axis caused by a misfit between the two subsystems. The CoO₂ sheets belong to a strongly correlated electron system that serve as electronic transport layers, whereas the Ca₂CoO₃ layers are insulating layers. The chemical formula can be written as [Ca₂CoO₃]RS [CoO₂]_{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 CdI2-type structure. The typical space group for this phase is C2/m and cell parameters are a \approx 4.8 Å, $c \approx$ 10.83 Å, $b1 \approx$ 4.55 Å and $b2 \approx 2.82$ Å, and $\beta \approx 98^{\circ}$. The Ca₃Co₄O₉ phase exhibits strong texture [12] and anisotropic thermoelectric properties in the abplane [5].

 $Co_3Co_2O_6$ has a space group of *R*-3*c*, with a = 9.0793(7) Å and c = 10.381(1) Å [39] (Fig. 3). This phase belongs to the n = 1 member of the homologous series, $A_{n+2}B_nB'O_{3n+3}$ (where A is an alkali-earth

(1)

¹ Certain 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.



Fig. 1. Phase diagram of the CaO-½Dy₂O₃-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 Ca₃Co₄O₉ view along the [010] axis.

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



Fig. 3. Crystal structure of $Ca_3Co_2O_6$ (n = 1 member in $Ca_{n+2}Co_nCoO_{3n+3}$), showing the feature of linear chains of successive alternations of CoO_6 octahedron with CoO_6 prism.

trigonal prisms and CoO₆ octahedra along the hexagonal *c*-axis [38]. The linear Co₂O₆⁶⁻ chains consist of one CoO₆ octahedron alternating with one CoO₆ trigonal prism. Each Co₂O₆⁶⁻ chain is surrounded by six other chains which form a hexagonal arrangement. The members in $A_{n+2}Co_nCo'O_{3n+3}$ can also be considered as ordered intergrowth between the $n = \infty$ (ACoO₃) and n = 1 (A₃Co₂O₆) end members [6,40].

$$CaO-Dy_2O_3 \text{ and } Dy_2O_3-Co_3O_4 \tag{2}$$

At 885 °C, no intermediate phases form in the CaO-Dy₂O₃ system



Fig. 4. Temperature dependence of power factor for $Ca_{3-x}Dy_xCo_4O_{9+d}$ (x = 0.00, 0.02, 0.05, and 0.10) samples [45] (Figure reuse permission obtained from J. Alloy and Compounds).

other than the $(Dy_{1-x}Ca_x)O_{3-z}$ ($0 \le x \le 0.075$) solid solution. The $(Dy_{1-x}Ca_x)_2O_{3-z}$ phase crystallizes in a monoclinic structure [41]. We found the solubility of Dy_2O_3 in CaO to be negligible at 885 °C. The only phase found in the Dy_2O_3 -CoO_z system was the $DyCoO_3$ phase which has the perovskite structure with space group *Pnma*, a = 5.410 Å, b = 7.397 Å, and c = 5.170 Å (PDF: 4-013-4303) [33,42]. The R_2CoO_4 (R = Dy) phase could not be prepared under the current conditions.

3.2. Ternary oxide system, CaO- 1/2Dy₂O₃-CoO_x

The CaO- $\frac{1}{2}$ Dy₂O₃-CoO_z phase diagram is a relatively simple diagram as compared with other analogs with larger size of R, namely, with R = La, Nd, Sm, Eu and Gd [23–27]. Undobutedly the size of the lanthanides is a major factor governing the phase formation in these systems.

Only one ternary solid solution phase was found in this system, namely, $(Ca_{3-x}Dy_x)Co_4O_{9-z}$ ($0 \le x \le 0.6$). The thermoelectric properties of this solid solution have been investigated extensively (Nong et al. [43]; Bhaskar et al. [44]; Wang et al. [45]) (Fig. 4), and Wang et al. [46]]. Bhaskar et al. reported the thermoelectric properties of the solid solution series $(Ca_{3-x}Dy_x)Co_4O_{9-z} x = 0, 0.02, 0.05, and 0.10$. In general, the electrical resistivity decreased and the thermopower increased with increasing Dy³⁺ content. Among the four samples, $Ca_{2,9}Dy_{0,10}Co_4O_{9+\delta}$ had the highest ZT of 0.044 at 300 K. Wang et al. [45] reported that substitution of Dv bv Ca resulted in increasing of both Seebeck coefficient and electrical resistivity in (Ca_{3-x}Dy_x)Co₄O_{9-z} due to the decrease of carrier concentration. Among the (Ca3- $_{x}Dy_{x})Co_{4}O_{9-z}$ (x = 0, 0.15, 0.3 and 0.5) members, x = 0.3 has the lowest lattice thermal conductivity, leading to a FOM of 0.27 at 1000 K. Nong et al. [43] found that among the series of (Ca_{3-x}R_x)Co₄O_{9-z} (R = Dy, Er, Ho and Lu) that they studied, the sample (Ca_{0.8}Lu_{0.2})Co₄O_{9-z} gave a FOM of 0.36 at 1073 K.

Results of Rietveld refinement confirmed absence of Ca-dopant in the Dy site of the DyCoO₃ phase. Furthermore, solid solution formation by substituting Dy at the Ca site in Ca₃Co₂O₆ was found to be negligible at 885 °C. It was reported earlier that the solid solution (Ca, R)₃Co₂O₆ was also absent in the CaO- $\frac{1}{2}$ R₂O₃-CoO_z systems (R = La, Nd, Sm, Eu and Gd [23–27]). However, (Ca_{3-x}Dy_x)Co₂O₆ was reported to form at a higher synthesis temperature of 1050 °C [47].

Another possible compound/solid solution in the CaO- $\frac{1}{2}R_2O_3$ -CoO_z system is a Ruddlesden-Popper family of compounds, $(R_{1-x}Ca_x)_2CoO_4$. Thorogood et al. (2011) [48] reported the structure, crystal chemistry and magnetism of a series of lanthanide R-rich calcium cobaltates: $R_{2-x}Ca_xCoO_{4+\delta}$. They found that when the size of R is large (R = La³⁺, Pr³⁺-Sm³⁺) or for compositions containing the smaller lanthanide ions



Fig. 5. Phase diagram of the CaO- 1/2Ga2O3 - CoOx system at 885 °C in air [27].



Fig. 6. Phase diagram of the CaO- $\frac{1}{2}La_2O_3$ - CoO_x system at 885 °C in air [23].

 $(< Gd^{3+} and Y^{3+} [27,49])$, the structure is tetragonal *I4/mmm* at room temperature; while R = Eu to Gd, the structure is orthorhombic *Bmab*. However, in this work the distorted K₂NiF₄-type Dy₂CoO₄₋₈ or (Dy, Ca)₂CoO₄₋₈ solid solution were confirmed to be absent.

3.3. Comparison of phase relationships in the CaO- $\frac{1}{2}La_2O_3$ -CoO_x CaO- $\frac{1}{2}Gd_2O_3$ -CoO_x and CaO- $\frac{1}{2}Dy_2O_3$ -CoO_x systems

It appears that the ionic size of the alkaline-earth and lanthanide ions governs the trend of phase formation, extent of solid solution formation of $(R_{1-x}Ca_x)CoO_{3-z}$, $(R_{1-x}Ca_x)_2O_{3-z}$, $(Ca_{3-x}R_x)Co_4O_{9-z}$, $(Ca_{3-x}D_x)Co_2O_6$ and $(R_{1+x}Ca_{1-x})CoO_{4-z}$, as well as the tie-line relationships in the CaO-1/2R₂O₃-CoO_z systems. Because of different phase formation and different range of solid solutions in the La-, Gd-, and the Dy-systems, the tie-line relationships are substantially different, leading to different appearance of the diagrams (Figs. 1 and 5, and 6).

In summary, all three diagrams contain the $(Ca_{3-x}R_x)Co_4O_{9-z}$ solid solution, the stoichiometric $Ca_3Co_2O_6$ phase, and the solid solutions $(R_{1-x}Ca_x)_2O_{3-z}$, and $(R_{1-x}Ca_x)CoO_{3-z}$ perovskite (except when R = Dy, it is a point compound). Furthermore, while all these systems contain the perovskite $RCoO_3$ phase, the structures of $LaCoO_3$, $GdCoO_3$, and $DyCoO_3$ are different from each other. The $(La_{1-x}Ca_x)CoO_3$ phase is rhombohedral with a space group *R-3c*, but $(Gd_{1-x}Ca_x)CoO_3$ and $DyCoO_3$ are orthorhombic with a space group *Pnma*. Among the three systems, the Ruddlesden-Popper phase $RCaCoO_{4-z}$ was found to be stable only in the $CaO-\frac{1}{2}Gd_2O_3-CoO_z$ system.

Because of the difference in phase formation in these three systems, the tie-line relationships are substantially different as well. In the Lasystem (Fig. 6), there are a total of four three-phase regions, and four two-phase tie-line bundles [23]. In the Dy-system, there are four three-phase regions and three two-phase tie-line bundles. However, a greater number of three-phase regions (six) and two-phase tie-line bundles (five) were found in the Gd-system (Fig. 5) due to the presence of the

additional GdCaCoO_{4-z} phase [27].

4. Summary

The phase diagram of the CaO- $\frac{1}{2}$ Dy₂O₃-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 thermoelectric properties. The diagram of the CaO- $\frac{1}{2}$ Dy₂O₃-CoO_z system is distinctively different from that determined for the CaO- $\frac{1}{2}$ La₂O₃-CoO_z and the CaO- $\frac{1}{2}$ Gd₂O₃-CoO_z systems. The homogeneity range of the low-dimensional phase, (Ca, Dy)₃Co₄O₉ (with a misfit layered structure), was established. The distorted perovskite-related phase, (Dy, Ca)_{n+2}Co_nCo'O_{3n+3} (with one dimensional cobalt oxide chains) was determined to be a stoichiometric compound, DyCoO₃. As the best cobaltate materials for thermoelectric applications, at present, are still the Ca₃Co₄O₉ type of compounds that feature misfit layered structure, we plan to continue to determine the phase diagrams of the CaO- R₂O₃-CoO_z systems, with R = Pr, Ho, Er, and Yb, in the near future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solidstatesciences.2018.12.010.

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