Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: http://www.elsevier.com/locate/ssscie

Crystal chemistry and phase equilibria of the CaO- $\frac{1}{2}$ Ho₂O₃-CoO_z system at 885 °C in air



^a Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

^b NCNR, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

^c Advanced Photon Source, Argonne National Laboratory, Argonne, IL, 60439, USA

^d Department of Chemistry, North Central College, Naperville, IL, 60540, USA

ARTICLE INFO

Keywords: Phase diagram of CaO- $\frac{1}{2}$ Ho₂O₃-CoO₂ at 885 °C in air Thermoelectric oxide (Ca_{3-x}Ho_x)Co₄O_{9-z} Phase compatibility relationships Structure for (Ho_{1-x}Ca_x)O_{(3-z)/2}

ABSTRACT

The phase equilibrium diagram of the CaO-½Ho₂O₃-CoO_z system was determined at 885 °C in air. This diagram offers compatibility relationships in the ternary oxide system that are essential for processing and for the understanding of properties of several thermoelectric phases in the system. Four three-phase regions and three solid solution tie-line regions were determined in the CaO-½Ho₂O₃-CoO_z system. In the CaO-Ho₂O₃ system, while a small solid solution region was identified for $(Ho_{1-x}Ca_x)O_{(3-z)/2}$ ($0 \le x \le 0.14$), Ho was not present in the Ca site of CaO. Neither the reported Ho₂CoO₄ phase in the Ho₂O-CoO₂ system nor the Ca-doped $(Ho_{1-x}Ca_{1-x})COA_{4-z}$ phase was present at 885 °C. No solid solution of the distorted perovskite, $(Ho_{1-x}Ca_x)COO_{3-z}$, was established at this temperature. The CaO-CoO₂ system consists of two calcium cobaltate thermoelectric compounds. The 2D thermoelectric oxide, $(Ca_{3-x}Ho_x)CoA_{9-z}$ ($0 \le x \le 0.5$), has a misfit layered structure, and the 1D Ca₃Co₂O₆ consists of chains of alternating CoO₆ trigonal prisms and CoO₆ octahedra. Ca₃Co₂O₆ was found to be a stoichiometric compound. A comparison of the phase diagrams of the CaO-½R₂O₃-CoO_z (R = La, Nd, Eu, and Ho) systems is given.

1. Introduction

In recent years, we have been in the midst of an energy crisis where soaring energy demand has been one of the greatest concerns. Thermoelectric (TE) ceramics have become increasingly important for their potential use in energy conversion and thermoelectric harvesting. However, despite world-wide intense research of TE materials, only a small number of materials have been found to have practical industrial applications because of the low efficiency of most materials. TE candidates need to have high electrical conductivity, low thermal conductivity and must maintain a temperature gradient to be considered useful. 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 *S* is the Seebeck coefficient or thermopower, σ is the electrical conductivity ($\sigma = 1/\rho$, ρ is electrical resistivity), κ is the thermal conductivity, and *T* is the absolute temperature, [1]. However, due to the interdependence of *S*, ρ , and κ , optimizing the *ZT* value remains a formidable task.

Oxide materials such as $Ca_3Co_4O_9$ [2–6,13,14], $NaCoO_x$ [7], $Ca_2Co_3O_6$ [8,9], $Bi_2Sr_2Co_2O_x$ [10], and the natural superlattices (Bi, A)

E-mail address: winnie.wong-ng@nist.gov (W. Wong-Ng).

* Corresponding author.

https://doi.org/10.1016/j.solidstatesciences.2020.106348 Received 3 June 2020; Accepted 26 June 2020 Available online 2 July 2020 1293-2558/Published by Elsevier Masson SAS. Cu₂Se₂O (A = Pb, Ba, Sr, and Ca) [11,12]) have been considered as candidates for waste heat conversion applications partly because of their stability at high temperature. The misfit layered compound Ca₃Co₄O₉ is among the oxides with the highest *ZT* [13,14]. Efforts on improving the thermoelectric properties of this material with dopants either on the Ca site or on the Co site have been conducted extensively [15–23].

Phase equilibrium diagrams are important for material designing and understanding materials properties. They also provide blue-prints for processing and understanding phase relationships. Phase diagrams of the (Ba, Sr, Ca)O-CoO_z, CaO-(Co,Zn)O_z and CaO- $\frac{1}{2}R_2O_3$ -CoO_z (R = lanthanide) systems are of high interest to the thermoelectric research community. We have previously reported the phase diagrams for CaO-SrO-CoO_z [15], CaO-ZnO-CoO_z [30], and CaO- $\frac{1}{2}R_2O_3$ -CoO_z (R = La [24], Nd [25], Sm [26], Eu [27], Gd [28], Dy [29]) systems. From these results, we found that the ionic size of the rare-earth ions plays an important role on phase compatibility and phase formation.

The first goal of this study is to establish the phase compatibility relationships, crystal chemistry, and crystallography of compounds in the CaO- $\frac{1}{2}$ Ho₂O₃-CoO_z system at 885 °C. The second goal is to study the





possible and range of formation of solid solutions of $(Ca_{1.x}Ho_x)_3Co_4O_{9-z}$, $(Ho_{1-x}Ca_x)CoO_{3-z}$, $(Ca_{1-x}Ho_x)_2Co_3O_6$, and $(Ca_{1.x}Ho_x)O_{(3-z)/2}$ using X-ray diffraction. The third goal is to compare the phase formation and phase relationships between the CaO- $\frac{1}{2}La_2O_3$ -CoO_z [24], CaO- $\frac{1}{2}Nd_2O_3$ -CoO_z [25], CaO- $\frac{1}{2}Eu_2O_3$ -CoO_z [27], and the current CaO- $\frac{1}{2}Ho_2O_3$ -CoO_z systems. The fourth goal of the study is to determine X-ray reference diffraction pattern(s) [31,32] of selected members of the (Ho_{1-x}Ca_x) O_{(3-z)/2}, (Ho_{1-x}Ca_x)CoO_{3-z}, (R_{1-x}Ca_x)₂CoO₄, and (Ca_{1-x}Ho_x)₂Co₃O₆ solid solution series, if they are confirmed to be stable at 885 °C. These reference pattern(s) will be included in the ICDD Powder Diffraction File (PDF [33]).

2. Experimental

2.1. Sample preparation

The samples were prepared using high temperature solid-state synthesis techniques. Table 1 gives the thirty-six samples that were prepared from a stoichiometric mixture of CaCO₃, Co₃O₄ and Ho₂O₃ (purity of samples are all greater than 99%). These samples were mixed, pelletized, and annealed at 750 °C for one day, and subsequently annealed at 825 °C, 850 °C, and 885 °C with intermediate grindings and pelletizations for another two to three weeks. The heat-treatment process was repeated until the powder X-ray diffraction patterns showed no further changes were detected.

2.2. X-ray diffraction

Powder X-ray diffraction was used to establish phase purity of the

Table 1

Thirty-six samples (mole fraction, %) prepared for the phase equilibria study of the CaO-½Ho₂O₃-CoO_z system at 885 °C in air. In this table, Ca =CaO; Ho = ½Ho₂O₃; Co = $\frac{1}{3}$ Co₃O₄.

	Са	Но	Со
#1	5	95	0
#2	4	96	0
#3	7.5	92.5	0
#4	10	90	0
#5	12.5	87.5	0
#6	15.0	85.0	0
#7	17.5	82.5	0
#8	20.0	80.0	0
#9	98.0	2.0	0
#10	99.0	1.0	0
#11	95	5	0
#12	33.333	33.333	33.333
#12	30.0	36.667	33.333
#14	58	2	40
#15	56	4	40
#16	54	6	40
#17	52	8	40
#18	35	25	40
#19	5	45	50
#20	10	40	50
#21	7.5	42.5	50
#22	15	35	50
#23	12.5	37.5	50
#24	41.43	1.43	57.14
#25	40	2.86	57.14
#26	38.57	4.29	57.14
#27	37.14	5.72	57.14
#28	35.72	7.14	57.14
#29	34.29	8.57	57.14
#30	32.86	10.00	57.14
#31	45	40	15
#32	5	75	20
#33	65	10	25
#34	30	20	50
#35	2	38	60
#36	20	15	65

samples and phase relationships among the phases prepared. Powder diffraction experiments were carried out using a Phillips X-ray powder diffractometer¹ (Cu K_{α} radiation) that was equipped with a scintillation counter and a series of Soller slits. The 2 θ scanning range was from 10° to 65°, and the step interval was 0.03°. Phase identification was achieved using powder reference diffraction patterns of compounds in the CaO-½Ho₂O₃-CoO_z system in the PDF [33].

2.3. Rietveld refinements using synchrotron X-ray diffraction

High resolution synchrotron X-ray powder diffraction data was collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using a wavelength of 0.45788 Å. Discrete detectors covered a final angular range from 0° to 50°, with data points collected every 0.001° in 20 at a scan speed of 0.01°/s. The instrumental optics of 11-BM incorporate two platinum-striped mirrors and a double-crystal Si (111) monochromator, where the second crystal has an adjustable sagittal bend [34]. The diffractometer is controlled via EPICS [35]. A vertical Huber 480 goniometer positions 12 perfect Si (111) analyzers and 12 Oxford-Danfysik LaCl₃ scintillators, with a spacing of 2° in 20 [36]. Capillary samples are mounted by a robotic arm and spun at \approx 90 Hz.

Diffraction data are normalized to incident flux and collected while continually scanning the diffractometer 2 θ arm. A mixture of National Institute of Standard and Technology standard reference materials, Si (SRMTM 640c) and Al₂O₃ (SRMTM 676), was used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2 θ offset, and small detector wavelength differences, before merging the data into a single set of intensities evenly spaced in 2 θ .

2.4. Powder diffraction reference pattern

Structure determination and reference diffraction pattern preparation were accomplished using the Rietveld refinement technique [37] with software suite GSAS-II by Toby and von Dreele [38]. Reference patterns were obtained with a Rietveld pattern decomposition technique. The reported peak intensities were derived from the extracted integrated intensities, and positions calculated from the lattice parameters. When peaks are not resolved at the resolution function, the intensities are summed, and an intensity-weighted d-spacing is derived and reported.

3. Results and discussion

Fig. 1 presents the phase diagram of the CaO-½Ho₂O₃-CoO_z system that was determined at 885 °C in air. The crystal chemistry and crystallography of various phases in the binary as well as the ternary oxide systems are discussed below. The phase relationships between solid solutions and other phases are expressed as tie-line bundles. From the current results, we found that among the several series of potential solid solutions, namely, $(Ho_{1-x}Ca_x)O_{(3-z)/2}$, $(Ho_{1-x}Ca_x)CoO_{3-z}$, $(Ca_{1-x}Ho_x)_3$. Co_4O_{9-z} , $(Ho_{1-x}Ca_x)_2CoO_{4-z}$, and $(Ca_{1-x}Ho_x)_2Co_3O_{6-z}$, only $(Ca_{1-x}Ho_x)_3$. Co_4O_{9-z} and $(Ho, Ca)_2O_3$ form solid solutions, $(Ho_{1-x}Ca_x)_2CoO_{4-z}$ is not stable at 885 °C, and the other two are point compounds. Crystal structure and reference powder pattern were determined for a selected member of the $(Ho_{1-x}Ca_x)O_{(3-z)/2}$ series, namely, $(Ho_{0.9}Ca_{0.1})O_{(3-z)/2}$. During the refinement process, Ho_2O_3 was used as the initial model. The Ho and Ca atoms were constrained to occupy the same site, with a total

¹ Certain trade names and company products including computer software 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- $\frac{1}{2}Ho_2O_3$ -CoO_x system at 885 °C in air, showing the limits of various solid solutions, and the tie-line relationships of various phases.

occupancy of unity.

3.1. Binary oxide systems

3.1.1. $CaO - CoO_z$

In the CaO-CoO_z system, the end member phases, CoO_z and CaO were found to be stoichiometric compounds. Ca₃Co₂O₆ and Ca₃Co₄O₉ are the only two binary oxide phases found in this system [3,4,8,9,14,39–44]. Ca₃Co₄O₉ is a misfit layered oxide that has two monoclinic subsystems with identical *a*, *c*, β , but different *b* values [3,4,14,40]. The first subsystem consists of triple rock-salt layers of Ca₂CoO₃ in the *ab* plane. The CoO₂ sheets belong to a strongly correlated electron system that serve as electronic transport layers, whereas the Ca₂CoO₃ layers are insulating layers. The second subsystem consists of a single CoO₂ layer, which has the CdI_2 -type structure (Fig. 2). There is an incommensurate spatial modulation along the *b*-axis caused by a misfit between the two subsystems. The typical space group for this phase is C2/m and cell parameters are a \approx 4.8 Å, $c \approx$ 10.83 Å, $b_1 \approx$ 4.55 Å and $b_2 \approx$ 2.82 Å, and $\beta \approx$ 98°. The Ca₃Co₄O₉ phase exhibits strong texture [13] and anisotropic thermoelectric properties in the ab-plane [6]. Tyson et al. [45] studied the local structure of Ca3Co4O9 using the density-functional theory





Fig. 3. (a)Crystal structure of $\rm Ca_3Co_2O_6~(n=1~member~in~Ca_{n+2}Co_nCoO_{3n+3})$ showing the feature of linear chains of successive alternations of CoO_6 octa-hedron with CoO_6 prism.(b). Crystal structure of Ca_3Co_2O_6 showing each Co_2O_6^{6-} chain being surrounded by six other chains. These Co_2O_6^{6-} chains are separated by octa-coordinated Ca^{2+} ions.

(DFT) approach. They qualitatively determine the optimized 3D structure, and provide insight into the disorder situation about two distinct Co sites in this system. DFT results suggest that in the Ca2CoO3 rocksalt layer, chains of CoOx exist along the *a* axis. This chainlike structure will



Fig. 2. Structure of calcium cobaltite $Ca_3Co_4O_9$. The Rock-Salt (RS) subsystem is incommensurate with the CoO_2 subsystem. CoO_6 octahedra are highlighted in both subsystems [44]. Reuse of figure was approved by American Physical Society (Phy. Rev. B).

disrupt the lattice in the rocksalt layer and reduce the thermal conductivity, leading to a high figure of merit.

 $Co_3Co_2O_6$ (*R*-3*c* [42]) belongs to the n = 1 member of the homologous series, $A_{n+2}B_nB^{\circ}O_{3n+3}$ (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) (Fig. 3a). This series of compounds can be described as having 1-dimensional linear parallel $Co_2O_6^{6-}$ chains, built by successive alternating face-sharing CoO_6 trigonal prisms and CoO_6 octahedra along the hexagonal *c*-axis [41]. The linear $Co_2O_6^{6-}$ chains consist of one CoO_6 octahedron alternating with one CoO_6 trigonal prism. Each $Co_2O_6^{6-}$ chain is surrounded by six other chains which form a hexagonal arrangement (Fig. 3b).

3.1.2. $Ho_2O_3 - Co_3O_4$ and $CaO - Ho_2O_3$

At 885 °C, the only phase found in the Ho₂O₃-CoO_z system is the HoCoO₃ phase which has the perovskite structure with the space group *Pnma*, a = 5.416 Å, b = 7.335 Å, and c = 5.144 Å (PDF: 4-013-4304) [46]. The RCoO₃ phase has been considered as an interesting thermo-electric material [24–29]. The Ho₂CoO₄ phase could not be prepared under the current conditions.

No intermediate phases form in the CaO-Ho₂O₃ system other than the (Ho_{1-x}Ca_x)O_{(3-z)/2} (0 \leq x \leq 0.14) solid solution. The (Ho_{1-x}Ca_x)O_{(3-z)/2} phase crystallizes in a cubic structure [47,48]. Structure description of one of the solid solution members (x = 0.1) is described below. We found the solubility of Ho₂O₃ in CaO to be negligible at 885 °C.

3.1.2.1. Structure of $(Ho_{1-x}Ca_x)O_{(3-z)/2}$. The observed (crosses), calculated (solid line), and difference (bottom) XRD patterns for $(Ho_{0.9}Ca_{0.1})O_{(3-z)/2}$, as determined by the Rietveld analysis technique, are shown in Fig. 4. The difference pattern is plotted at the same scale as the other patterns. The row of tick marks refers to the calculated peak positions. The refinement residual R_{wp} , R_p , and goodness of fit values were found to be 5.24%, 3.83% and 1.08, respectively.

Tables 2 and 3 provide atomic coordinates and selected bond distances for $(H_{0_0,9}Ca_{0.1})O_{(3-z)/2}$, respectively. No impurity phase was found. $(H_{0_0,9}Ca_{0.1})O_{(3-z)/2}$ was determined to be isostructural with $H_{0_2}O_3$. The lattice parameters were found to be a = 10.609078 (7) Å, V = 1194.079 (3) Å³, Z = 16, $D_x = 8.19$ g/cm³. An increase of unit cell volume when the larger Ca^{2+} ($r_{Ca}^2 = 1.14$ Å [49]) ion was doped into the Ho-site ($r_{H_0}^{3+} = 1.04$ Å [49]) is expected (for $H_{0_2}O_3$, a = 10.6083 (6) Å, V = 1193.82 Å³, Z = 16, $D_x = 8.409$ g/cm³) [50].

The structure of $(Ho_{0.9}Ca_{0.1})_2O_{(3\cdot z)/2}$ belongs to the bixbyite type $[^{VI}A_2][^{IV}O_3]$, which is body-centered cubic, space group *Ia3*, Z = 16 [51]. There are two crystallographically nonequivalent Ho/Ca atoms ((Ho(1)/Ca (1) and Ho(2)/Ca (2)) and only one type of oxygen atom (O (3)). In (Ho_{0.9}Ca_{0.1})O_{(3\cdot z)/2}, Ca²⁺ is found to substitute Ho³⁺ in both 8(b) (¹/₄,¹/₄,¹/₄) and 24(d) (x, 0, ¹/₄) Wyckoff positions, and O²⁻ was found to be



is plotted at the same scale as the other patterns. The row of tick marks refers to

the calculated peak positions.

v

0

1501(1)

Atomic coordinates (x 104) and equivalent isotropic displacement parameters $(U(eq), Å^2)$ for $(Ho_{0.9}Ca_{0.1})O_{(3-2)/2}$. U(eq) is defined as one third of the trace of

the orthogonalized Uij tensor. a=10.60908(2) Å, V=1194.081 (6) Å³, Z=16, D_r

 $= 8.19 \text{ g/cm}^3$. 'HC' stands for the Ho/Ca site, and 'Occ' stands for occupancy.

The total occupancy of Ho and Ca at each HC site is 1.0. The occupancy for O(3)

z

2500

3805(2)

Table 2

is 1.001(1).

HC(1)

HC(2)

0(3)

х

-0322(1)

3924(2)

Table 3
Selected interatomic distances in $(Ho_{0.9}Ca_{0.1})O_{(3-z)/2}$.

Atom to atom	Distances [Å]				
O (3)-(Ho(1)/Ca (1))	2.3073 (12)				
O (3)-(Ho(2)/Ca (2))	2.257 (2)				
O (3)-(Ho(2)/Ca (2))	2.2395 (7)				
O (3)-(Ho(2)/Ca (2))	2.335 (2)				
(Ho(1)/Ca (1))-O (3) x6	2.3073 (12)				
(Ho(2)/Ca (2))-O (3) x2	2.257 (2)				
(Ho(2)/Ca (2))-O (3) x2	2.2395 (7)				
(Ho(2)/Ca (2))-O (3) x2	2.335 (2)				

in the 48(e) general positions. Both the Ho/Ca atoms are 6-fold coordinated (Fig. 5). Each Ho(1)/Ca(l) is surrounded by six equidistant oxygen atoms (2.3073 (12) Å) which lie nearly at the corners of a distorted cube with two body-diagonally opposite corners missing (Fig. 5). Each Ho(2) is also surrounded by six oxygen atoms which lie nearly at the corners of a distorted cube, except in this case two face-diagonally opposite corners are missing instead. There are three different sets (2 in each set) of Ho(2)/Ca (2)-O distances, namely, 2.257 (2) Å, 2.2395 (7) Å, and 2.335 (2) Å. The average of these six distances is 2.277 Å.

Fig. 6 gives the 3D structure of $(Ho_{0.9}Ca_{0.1})O_{(3-z)/2}$ with connected Ho/Ca–O bonds [52]. It also shows a distorted tetrahedral O-(Ho/Ca)₄ motif and a 6-fold coordinated (Ho/Ca)–O₆ motif. According to Caro [47] and Roth et al. [48], the bixbyite structure is best described based on close-pack arrangement of distorted O-M₄ tetrahedra (M = metal). In Fig. 7, the O (3) site can be considered as surrounded by three Ho(2)/Ca (2 sites (orange color) and one Ho(1)/Ca (1) site (green color).

From the results of neutron diffraction, the O (3) site is fully occupied (The *z* value in $(Ho_{0.9}Ca_{0.1})_2O_{(3-z)/2}$ is '0'). The computed chemical formula for the compound derived from the structure is $(Ho_{0.9\pm0.003}Ca_{0.095\pm0.003})_2O_3$, therefore agreeing with $(Ho_{0.9}Ca_{0.1})_2O_3$ within two σ 's.

3.1.2.2. Powder reference diffraction pattern of $(Ho_{0.9}Ca_{0.1})O_{3.z/2}$. The reference pattern of $(Ho_{0.9}Ca_{0.1})O_{3/z}$ is given in Table 4. In this pattern, the particular peak that has the strongest intensity in the entire pattern is assigned an intensity of 999 and other lines are scaled relative to this value. The symbols 'M' refers to peaks containing contributions from two reflections. The intensity values reported are integrated intensities (rather than peak heights) based on the corresponding profile parameters, and the *d*-spacing values are calculated values from refined lattice parameters. For peaks that are not resolved at the instrumental resolution, the intensity value are used. For resolved overlapped peaks, intensity-weighted calculated d-spacing, along with the observed integrated intensity and the *hkl* indices of both peaks (for 'M') are used. In the case of a cluster, often unconstrained profile fits reveal the presence

Solid State Sciences 107 (2020) 106348

Occ. of Ho

0.901(3)

U(eq)

0.00431(5)

0.00298(2)

0.0147(3)



Fig. 5. Schematic bixbyite structure of (Ho_{0.9}Ca_{0.1})O_{(3-2)/2}. The two crystallographic independent Ho/Ca atoms are inside two "distorted cubes".



Fig. 6. Crystal structure of $(Ho/Ca)_2O_3$ with connected Ho–O bonds (O-red spheres and (Ho/Ca)-grey spheres) [51]. Two basic building motifs are identified: the O(Ho/Ca)₄ and (Ho/Ca)O₆ units. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

of multiple peaks, even when they are closer than the instrumental resolution. In this situation, both *d*-spacing and intensity values are reported independently. The $(Ho_{0.9}Ca_{0.1})O_{(3/2)}$ pattern has been submitted for inclusion in the PDF.

3.2. II. Ternary oxide system, CaO- ½Ho₂O₃-CoO_x

It is known that size of the lanthanides is one of the major factors governing the phase formation in maaterials systems. There is no exception in the phase formation in the CaO- $\frac{1}{2}R_2O_3$ -CoO_z systems. The CaO- $\frac{1}{2}Ho_2O_3$ -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, Gd and Dy [24–29] due to different ionic size of R.

In the CaO-½Ho₂O₃-CoO_z system, only one ternary solid solution phase was found, namely, $(Ca_{3-x}Ho_x)Co_4O_{9-z}$ (0 $\leq x \leq$ 0.6). The thermoelectric properties of this solid solution have been investigated



Fig. 7. Crystal structure of $(Ho_{0.9}Ca_{0.1})O_{(3-z)/2}$ constructed using the O- $(Ho/Ca)_4$ tetrahedral motifs throughout. The green balls represent Ho(1) and the orange balls represent Ho(2). Each tetrahedron has three Ho(1) and one Ho(2) at the corners. The outline of the unit cell is also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

extensively [53–55]. In general, the electrical resistivity decreases and the thermopower increases with increasing Ho³⁺ content. The *ZT* values for all samples tend to increase with the increasing temperature and increasing Ho doping. Among $(Ca_{3-x}Ho_x)Co_4O_{9-z}$ (x = 0, 0.15, 0.3 and 0.5) members, x = 0.3 has the lowest lattice thermal conductivity and an increase of Seebeck coefficients, leading to the relatively largest *ZT* value among the four samples at 1000 K (Fig. 8) [55]. Nong et al. [56] found that among the (Ca_{3-x}R_x)Co₄O_{9-z} (R = Dy, Er, Ho, and Lu) series that they studied, the sample (Ca_{0.8}Lu_{0.2})Co₄O_{9-z} gave a high *ZT* of 0.36 at 1073 K.

Results of Rietveld refinement confirmed absence of Ca-dopant in the Ho site of the HoCoO₃ phase, despite in the systems with larger R have demonstrated solid solutions of Ca substituted into the R sites [24–28]. Furthermore, solid solution formation by substituting Ho at the Ca site in Ca₃Co₂O₆ was also found to be negligible at 885 °C. It was reported earlier that the solid solution (Ca, R)₃Co₂O₆ was also absent in the

Table 4

X-ray powder pattern for $(Ho_{0.9}Ca_{0.1})O_{(3-2)/2}$, Cubic a=10.60908(2) Å, V=1194.081 (6) Å³, Z=16. The symbols 'M' and '+' refer to peaks containing contributions from two and or more than two reflections, respectively. The particular peak that has the strongest intensity in the entire pattern is assigned an intensity of 999 and other lines are scaled relative to this value. The d-spacing values are calculated values from refined lattice parameters, and 'T' represents integrated intensity values.

d _{cal}	I _{obs}	h	k	1		d _{cal}	I _{obs}	h	k	1	
5.3045	5	2	0	0		4.3311	100	2	1	1	
3.0626	999	2	2	2		2.8354	19	3	1	2	М
2.8354	19	3	2	1	М	2.6523	361	4	0	0	
2.5006	57	4	1	1		2.3723	10	4	0	2	Μ
2.3723	10	4	2	0	М	2.2617	37	3	3	2	
2.1050	8	4	2	2	М	2.0806	90	4	1	3	M
2.0800	90 27	4	3 2	1	M	1.9309	441	4	4	2	IVI
1.8194	29	4	3	3	101	1.7682	6	6	0	0	
1.7210	59	6	1	1	+	1.6774	15	6	0	2	М
1.6774	15	6	2	0	М	1.6370	50	5	1	4	М
1.6370	50	5	4	1	Μ	1.5994	386	6	2	2	
1.5642	74	6	1	3	Μ	1.5642	74	6	3	1	Μ
1.5313	85	4	4	4		1.5004	30	5	3	4	Μ
1.5004	30	5	4	3	M	1.4712	15	6	0	4	м
1.4437	20	6	3	3	+ M	1.4177	20	6	2	4	111
1.3261	55	8	0	0	101	1.3059	52	8	1	1	+
1.2865	28	8	0	2	+	1.2680	31	6	3	5	M
1.2680	31	6	5	3	М	1.2503	19	8	2	2	
1.2333	51	8	3	1	+	1.2170	115	6	6	2	
1.2012	4	7	5	2		1.1861	90	8	0	4	М
1.1861	90	8	4	0	М	1.1716	15	8	3	3	
1.1576	16	8	2	4	М	1.1576	16	8	4	2	М
1.1440	36	7	1	6	+	1.1309	2	6	6	4	
1.1183	38	8	5	1	+	1.0942	30	2	0	3	+
1.0628	22	8	+ 6	4	м	1.0717	22	10	0	0	т М
1.0505	11	10	1	1		1.0403	47	8	2	6	+
1.0304	11	9	3	4	М	1.0304	11	9	4	3	M
1.0209	67	6	6	6	Μ	1.0209	67	10	2	2	М
1.0115	35	7	6	5	+	0.9936	30	8	5	5	+
0.9850	32	8	6	4	+	0.9767	22	10	3	3	+
0.9685	29	10	2	4	М	0.9685	29	10	4	2	М
0.9605	22	8	7	3	+	0.9451	23	9	3	6	+
0.9377	14	8 10	8 5	0	т	0.9234	13	0	4	4	+
0.9031	16	8	5 7	5	+	0.8966	38	10	2	6	M
0.8966	38	10	6	2	M	0.8903	7	9	5	6	М
0.8903	7	9	6	5	М	0.8841	18	8	8	4	М
0.8841	18	12	0	0	Μ	0.8780	21	9	1	8	+
0.8721	15	12	0	2	М	0.8721	15	12	2	0	М
0.8662	15	10	1	7	+	0.8605	21	12	2	2	+
0.8549	12	9	3	8	+	0.8440	17	11	6	1	+
0.8387	18	12	0	4	IVI	0.8387	18	12	4	0	IVI
0.8333	9 12	9	, 6	7	+	0.8185	23	10	8	2	т
0.8137	10	9	5	8	+	0.8089	6	10	6	6	
0.8043	7	10	7	5	+	0.7997	9	12	4	4	
0.7952	4	12	3	5	+	0.7908	29	10	4	8	+
0.7864	10	11	5	6	+	0.7821	22	12	2	6	М
0.7821	22	12	6	2	M	0.7779	12	11	1	8	+
0.7697	5	10	3	9	М	0.7697	5	10	9	3	M
0.7656	1	8	8	8	М	0.7617	18	9	8	/	+ M
0.7540	5	9	9	4	1VI +	0.7578	20	14	8	6	+
0.7464	2	12	3	7	M	0.7464	20	12	7	3	M
0.7428	12	10	10	2	М	0.7428	12	14	2	2	М
0.7392	15	13	6	1	+	0.7356	4	12	0	8	М
0.7356	4	12	8	0	М	0.7321	7	11	8	5	+
0.7286	12	14	0	4	+	0.7252	4	13	3	6	М
0.7252	4	13	6	3	M	0.7219	26	14	4	2	+
0.7185	5	11 12	9	4	+ M	0.7120	4	13	/	2	+ M
0.7069	3 4	12 9	4 9	0 8	1V1 +	0.7009	э 13	14 10	0 8	4 8	M
0.7026	13	14	4	4	M	0.6995	13	10	3	10	+
0.6965	4	14	0	6	M	0.6965	4	14	6	0	M
0.6935	12	11	8	7	+	0.6906	7	14	2	6	М
0.6906	7	14	6	2	М	0.6877	4	11	6	9	+
0.6820	7	13	8	3	+	0.6792	13	12	6	8	М
0.6792	13	12	10	0	Μ	0.6764	4	11	5	10	М
0.6764	4	11	10	5	Μ	0.6737	26	12	2	10	+

(continued on next page)

W. Wong-Ng et al.

Table 4 (continued)

d_{cal}	I _{obs}	h	k	1		d_{cal}	I _{obs}	h	k	1	
0.6710	3	15	3	4	+	0.6657	5	13	6	7	+
0.6631	2	16	0	0		0.6605	5	13	8	5	+
0.6580	27	12	10	4	+	0.6554	3	10	9	9	+
0.6529	22	14	8	2	+	0.6505	7	11	8	9	+
0.6481	1	14	6	6		0.6457	8	15	3	6	+
0.6433	4	16	0	4	+	0.6409	2	12	9	7	+
0.6386	21	14	4	8	+	0.6340	9	12	10	6	Μ
0.6318	2	13	7	8	Μ	0.6318	2	13	8	7	Μ
0.6273	4	15	6	5	+	0.6252	2	16	4	4	
0.6230	4	15	8	1	+	0.6280	5	16	0	6	Μ
0.6280	5	16	6	0	Μ	0.6187	2	13	10	5	+
0.6166	18	16	2	6	+	0.6146	2	15	3	8	Μ
0.6146	2	15	8	3	Μ	0.6105	2	11	9	10	+
0.6065	3	11	11	8	+	0.6045	12	12	10	8	+
0.6026	2	15	6	7	Μ	0.6026	2	15	7	6	Μ
0.5987	6	13	9	8	+	0.5949	2	13	7	10	+
0.5912	2	13	3	12	+	0.5894	5	14	8	8	+
0.5876	5	15	1	10	+	0.5858	7	16	6	6	+
0.5822	3	18	2	2		0.5805	3	17	6	3	+
0.5771	2	15	7	8	+	0.5754	10	14	0	12	+
0.5737	3	15	6	9	+	0.5720	21	14	12	2	+
0.5671	4	17	6	5	+	0.5639	5	17	1	8	+
0.5623	21	14	4	12	+	0.5592	13	16	2	10	+
0.5576	3	17	8	3	+	0.5561	3	18	2	6	Μ
0.5561	3	18	6	2	Μ	0.5515	2	15	9	8	+
0.5501	7	16	10	4		0.5486	4	15	7	10	+
0.5471	10	14	12	6	+	0.5457	3	17	8	5	+
0.5428	1	15	1	6	+						



Fig. 8. Temperature dependence of ZT for $Ca_{3-x}Ho_xCo_4O_{9+d}$ (x = 0.0, 0.15, 0.3, and 0.45) [54].

CaO-½R₂O₃-CoO_z systems (R = La, Nd, Sm, Eu, Gd and Dy [24–29]. However, (Ca_{3-x}Ho_x)Co₂O₆ was reported to exist as a solid solution at a higher synthesis temperature of 1000 °C [56].

Another possible compound/solid solution in the CaO-½R₂O₃-CoO_z system is a Ruddlesden-Popper family of compounds, $(R_{1-x}Ca_x)_2CoO_{4-z}$. Thorogood et al. [23]. 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 $(R = La^{3+}, Pr^{3+}-Sm^{3+})$ or for compositions containing the smaller lanthanide ions ($<Gd^{3+}$ and Y^{3+} [23,28]) the structure is tetragonal *I4/mmm* at room temperature; while R = Eu to Gd, the structure is orthorhombic *Bmab*. However, in the CaO-½R₂O₃-CoO_z system the distorted K₂NiF₄-type Ho₂CoO_{4+ $\delta}$ or (Ho, Ca)₂CoO_{4-z} solid solution were confirmed to be absent.}</sub>

In the CaO- $\frac{1}{2}$ Ho₂O₃-CoO_x system, there are a total of four three-

phase regions and three tie-line bundles. These tie-line bundles are defined by $CoO_z\text{-}(Ca_{3-x}Ho_x)Co_4O_{9-z}$; $Ca_3Co_2O_6\text{-}(Ca_{3-x}Ho_x)Co_4O_{9-z}$; and $HoCoO_{3-z}\text{-}^{1/2}(Ho,Ca)_2O_3$. The four three-phase regions are defined by CoO_z - $HoCoO_{3-z}$ -($Ca_{2.50}Ho_{0.50}$)Co_4O_{9-z}; $HoCoO_{3-z}$ - ($Ca_{2.50}Ho_{0.50}$)Co_4O_{9-z}; $HoCoO_{3-z}$ - ($Ca_{2.50}Ho_{0.50}$)Co_4O_{9-z} - ($Ca_{2.50}Ho_{0.50}$)Co_4O_{9-z}

3.3. Comparison of phase relationships in the CaO- $\frac{1}{2}La_2O_3$ -CoO_x, CaO- $\frac{1}{2}Nd_2O_3$ -CoO_x, CaO- $\frac{1}{2}Eu_2O_3$ -CoO_x, and CaO- $\frac{1}{2}Ho_2O_3$ -CoO_x systems

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}, $(R_{1-x}Ca_x)O_{(3-z)/2}$, $(Ca_{3-x}R_x)Co_4O_{9-z}$, $(Ca_{3-x}Ho_x)Co_2O_6$ and $(R_{1+x}Ca_{1-x})CoO_{4-z}$, as well as the tie-line relationships in the CaO- $\frac{1}{2}R_2O_3$ -CoO_z systems. Because of different phase formation and different range of solid solutions in the La-, Nd-, Eu-, and the Ho-systems, the tie-line relationships are expected to be different, leading to different appearance of these diagrams (Fig. 1, Fig. 9, Fig. 10, and Fig. 11).

All four diagrams contain the stoichiometric $Ca_3Co_2O_6$ phase, the $(Ca_3._xR_x)Co_4O_{9-z}$ solid solution, and the solid solutions $(R_{1-x}Ca_x)_2O_{3-z}$, and $(R_{1-x}Ca_x)CoO_{3-z}$ perovskites (except when R = Ho, it is a point compound). Furthermore, while all these systems contain a perovskite RCoO₃ phase (potential thermoelectric materials), the structures of LaCoO₃, NdCoO₃, EuCoO₃, and HoCoO₃ are different from each other. The $(Nd_{1-x}Ca_x)CoO_3$, $(Gd_{1-x}Ca_x)CoO_3$ and HoCoO₃ are orthorhombic with a space group *Pnma*, while the $(La_{1-x}Ca_x)CoO_3$ phase is rhombohedral with a space group *R-3c*. Among the four systems, the Ruddlesden-Popper phase RCaCoO_{4-z} was found to be stable only in the CaO- $\frac{1}{2}Nd_2O_3$ -CoO_z and CaO- $\frac{1}{2}Eu_2O_3$ -CoO_z systems.

Because of the difference in phase formation in these three systems, the tie-line relationships are substantially different as well. In the Lasystem (Fig. 9), there are a total of four three-phase regions, and four two-phase tie-line bundles [24]. In the case of the R = Nd system, there are a total of six three-phase regions and six tie-line bundles [25]. In the R = Eu system, there are a total of six three-phase regions and five tie-line bundles [27]. However, in the Ho-system (Fig. 1), there are only four three-phase regions and three two-phase tie-line bundles, due to the absence of the RCaCoO_{4-z} phase.



Fig. 9. Phase diagram of the CaO- ½La₂O₃ - CoO_x system at 885 °C in air [24].



Fig. 10. Phase diagram of the CaO- ${}^{\prime}\!_2Nd_2O_3$ - CoO_x system at 885 °C in air [25].

4. Summary

The phase diagram of the CaO-½R₂O₃-CoO_z (R = Ho) system was determined at 885 °C in air. This diagram is distinctively different from those determined for the CaO-½La₂O₃-CoO_z, CaO-½Nd₂O₃-CoO_z and the CaO-½Eu₂O₃-CoO_z systems as the ionic size of R is one of the important factors that determines phase formation. The homogeneity range of the low-dimensional phase, (Ca, Ho)₃Co₄O_{9-z} which has a misfit layered structure was established. The distorted perovskite-related phase, (Ca, Ho)_{n+2}Co_nCo'O_{3n+3} (with one dimensional cobalt oxide chains) was determined to be a stoichiometric compound, Ca₂CoO₃, with n = 0. Up to present, one of the best cobaltate materials for thermoelectric applications, is still the (Ca, R)₃Co₄O₉ type of compounds that feature misfit layered structure, we plan to continue to develop the phase diagrams of the CaO-R₂O₃-CoO_z systems, with R = Pr, Er, and Yb in the near future.



Fig. 11. Phase diagram of the CaO- ½Eu₂O₃ - CoO_x system at 885 °C in air [27].

Declaration of competing interest

None

CRediT authorship contribution statement

W. Wong-Ng: Conceptualization, Formal analysis, Supervision, Writing - original draft. W. Laws: Data curation, Methodology. Q. Huang: Formal analysis, Methodology. J. Hou: Formal analysis. S.H. Lapidus: Data curation, Software. L. Ribaud: Data curation, Software. J.A. Kaduk: Formal analysis, Writing - review & editing.

Acknowledgements

Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. ICDD is thanked for the partial support through the Grantsin-Aid program, Grant No. 0903.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solidstatesciences.2020.106348.

References

- G.S. Nolas, J. sharp, H.J. GoldSmid, Thermoelectrics: Basic Principles and New Materials Developments, Springer, New York, 2001.
- [2] D. Grebille, S. Lambert, F. Bouree, V. Petricek, J. Appl. Crystallogr. 37 (2004) 823–831.
- [3] A.C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, J. Hejmunck, Phys. Rev. B 62 (2000) 166–175.
- [4] B. Zan, J.L. Lan, Y.C. Liu, J.X. Ding, Y.H. Lin, C.W. Nan, J. Inorg. Mater. 29 (3) (2014) 237–244.
- [5] H. Minami, K. Itaka, H. Kawaji, Q.J. Wang, H. Koinuma, M. Lippmaa, Appl. Surf. Sci. 197 (2002) 442–447.
 - [6] Y.F. Hu, W.D. Si, E. Sutter, Q. Li, Appl. Phys. Lett. 86 (2005), 082103.
 - [7] I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B 56 (1997) 12685–12687.
 [8] M. Mikami, R. Funahashi, M. Yoshimura, Y. Mori, T. Sasaki, J. Appl. Phys. 94 (10) (2003) 6579–6582.
 - [9] M. Mikami, R. Funahashi, J. Solid State Chem. 178 (2005) 1670-1674.
 - [10] S.F. Wang, A. Venimadhav, S.M. Guo, K. Chen, Q. Li, A. Soukiassian, D.G. Schlom, M.B. Katz, X.Q. Pan, W. Wong-Ng, M.D. Vaudin, X.X. Xi, Appl. Phys. Lett. 94 (2009), 022110.
 - [11] W. Wong-Ng, Y. Yan, J.A. Kaduk, X.F. Tang, Powder Diffr. 31 (3) (2016) 223-228.

- [12] W. Wong-Ng, Y. Yan, J.A. Kaduk, X.F. Tang, Solid State Sci. 72 (2017) 55–63.
- [13] W. Wong-Ng, M.D. Vaudin, M. Otani, N.D. Lowhorn, Y.F. Hu, Q. Li, B. He, J. Appl. Phys. 102 (3) (2007) 33520.
- [14] M. Shikano, R. Funahschi, Appl. Phys. Lett. 82 (2003) 1851–1853.
- [15] W. Wong-Ng, G. Liu, J. Martin, E. Thomas, N. Lowhorn, J.A. Kaduk, J. Appl. Phys. 107 (2010), 033508.
- [16] W. Wong-Ng, T. Luo, M. Xie, W.H. Tany, J.A. Kaduk, Q. Huang, Y. Yan, S. Chattopadhyay, X. Tang, T. Tritt, J. Solid State Chem. 184 (8) (2011) 2159–2166.
- [17] S. Li, R. Funahashi, I. Matsubara, K. Ueno, S. Sodeoka, H. Yamada, Chem. Mater. 12 (2000) 2424–2427.
- [18] M. Prevel, O. Perez, J.G. Noudem, Solid State Sci. 9 (2007) 231–235.
- [19] T. Takami, H. Ikuta, U. Mizutani, Jap. J. Appl. Phys. 43 (No 12) (2004) 8208-8212.
- [20] S. Li, R. Funahashi, I. Matsubara, H. Yamada, K. Ueno, S. Sodeoka, Ceram. Int. 27 (2001) 321–324.
- [21] M. Otani, N.D. Lowhorn, P.K. Schenck, W. Wong-Ng, M.L. Green, K. Itaka, H. Koinuma, Appl. Phys. Lett. 91 (2007) 132102.
- [22] M. Otani, K. Itaka, W. Wong-Ng, P.K. Schenck, H. Koinuma, Surf. Sci. 254 (2007) 765–767.
- [23] G.J. Thorogood, P.-Y. Orain, M. Ouvry, B. Piriou, T. Tedesco, K.S. Wallwork, J. Herrmann, M. James, Solid State Sci. 13 (12) (2011) 2113–2123.
- [24] W. Wong-Ng, W. Laws, Y.G. Yan, Solid State Sci. 17 (2013) 107-110.
- [25] W. Wong-Ng, W. Laws, K.R. Talley, Q. Huang, Y. Yan, J. Martin, J.A. Kaduk, J. Solid State Chem. 215 (2014) 128–134.
- [26] W. Wong-Ng, W. Laws, S.H. Lapidus, J.A. Kaduk, Solid State Sci. 48 (2015) 31-38.
- [27] W. Wong-Ng, W. Law, J.A. Kaduk, Solid State Sci. 58 (2016) 105–110.
- [28] W. Wong-Ng, W. Laws, S. Lapidus, L.L. Ribaud, J.A. Kaduk, Solid State Sci. 72 (2017) 47–54.
- [29] W. Wong-Ng, W. Laws, J.A. Kaduk, Solid State Sci. 88 (2019) 57-62.
- [30] W. Wong-Ng, T. Luo, W. Xie, W.H. Tang, J.A. Kaduk, Q. Huang, Y. Yan,
- S. Chattopadhyay, X. Tang, T. Tritt, J. Solid State Chem. 184 (8) (2011) 2159.
 [31] H.F. McMurdie, M.C. Morris, E.H. Evans, B. Paretzkin, W. Wong-Ng, Powder Diffr.
- 1 (1) (1986) 40. [32] H.F. McMurdie, M.C. Morris, E.H. Evans, B. Paretzkin, W. Wong-Ng, L. Ettlinger, C.
- R. Hubbard, Powder Diffr. 1 (2) (1986) 66–76.
 [33] Powder Diffraction File (PDF), International Centre for Diffraction Data (ICDD), 12
- Campus Blvd., Newtown Square, PA 19073-3273. [34] J. Wang, B.H. Toby, P.L. Lee, L. Ribaud, L, S.M. Antao, C. Kurtz, M. Ramanathan, R.
- B. Von Dreele, M.A. Beno, Rev. Sci. Instrum. 79 (2008), 085105.

[35] L.R. Dalesio, J.O. Hill, M. Kraimer, S. Lewis, D. Murray, S. Hunt, W. Watson, M. Clausen, J. Dalesio, Nuclear Instruments & Methods in Physics Research Section

Solid State Sciences 107 (2020) 106348

- A. Accelerators Spectrometers Detectors and Associated Equipment 352 (1994) 179–184.
 [36] P.L. Lee, D. Shu, M. Ramanathan, C. Preissner, J. Wang, M.A. Beno, R.B. Von
- Dreele, L. Ribaud, C. Kurtz, S.M. Antao, X. Jiao, B.H. Toby, J. Synchrotron Radiat. 15 (2008) 427–432.
- [37] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65-71.
- [38] B.H. Toby, R.B. Von Dreele, GSAS-II: the genesis of a modern open-source all purpose crystallography software package, J. Appl. Crystallogr. 46 (2) (2013) 544–549.
- [39] E. Woermann, A. Muan, J. Inorg. Nucl. Chem. 32 (5) (1970) 1455-1459.
- [40] B. Raveau, M. Seikh, Wiley Online Library. Wiley-VCH Verlag Gmbh & Co. KGaA, 2012. https://application.wiley-vch.de/books/sample/3527331476_c01.pdf.
- [41] T. Takami, H. Ikuta, U. Mizutani, Jap. J. Appl. Phys. 43 (12) (2004) 8208–8212.
 [42] H. Fjellvag, E. Gulbrandsen, S. Aasland, A. Olsen, B.C. Hauback, J. Solid State
- Chem. 124 (1996) 190–199. [43] K. Boulahya, M. Parras, J.M. González-Calbet, J. Solid State Chem. 145 (1999) 116–127.
- [44] S. Lemal, J. Varignon, D. Bilc, P. Ghosez, Phys. Rev. B95 (2017), 075205.
- [45] T.A. Tyson, Z. Chen, Q. Jie, Q. Li, J.J. Tu, Phys. Rev. B79 (2009) 1–7, 024109.
- [45] I.A. Iyson, Z. Chen, Q. Jie, Q. Li, J.J. Tu, Filys. Rev. *B* 9 (2009) 1–7, 024109.
 [46] J.A. Alonso, M.J. Martinez-Lope, C. de la Calle, Y. Pomjakushin, J.A. Alonso, M. J. Martinez-Lope, C. de la Calle, Y. Pomjakushin, J. Mater. Chem. 16 (2006) 1555–1560.
- [47] P.E. Caro, J. Less Common. Met. 16 (1968) 367.
- [48] R.S. Roth, S.J. Schneider, Phase equilibria in systems involving the rare-earth oxides. Part 1. Polymorphism of the oxides of the trivalent rare-earth ions, J. Res. Natl. Bur. Stand. 64A (1960) 309.
- [49] R.D. Shannon, Acta Crystallogr. A32 (1976) 751-767.
- [50] B. Antic, M. Mitric, D. Rodic, J. Magnet, Mag. Mater. 145 (1995) 349-356.
- [51] L. Pauling, M.D. Shappell, Z. Kristallogr. 75 (1930) 128.
- [52] Orci Eigenes Werk (own work), Data source: M. Marezio: refinement of the crystal structure of In₂O₃ at two wavelengths, in: Acta Cryst vol. 20, 1966, pp. 723–728. CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=7178684.
- [53] N.V. Nong, C.-Y. Liu, M. Ohtaki, J. Alloys Compd. 509 (3) (2011) 977–981.[54] Yang Wang, Luxiang Xu, Sui Yu, Xianjie Wang, Jinguang Cheng, Wenhui Su, Appl.
- Phys. Lett. 97 (2010), 062114.
- [55] T. Zhu, J. Zhou, Adv. Mater. Res. 228-229 (2011) 947.
- [56] N.V. Nong, M. Ohtaki, Solid State Commun. 139 (2006) 232-234.