Chemistry of Metals and Alloys

Chem. Met. Alloys 17 (2024) 32-37
Ivan Franko National University of Lviv
http://publications.lnu.edu.ua/chemetal

The Ca–Tb–Co–O system: phase diagram and crystal structures

Oksana ZAREMBA[1]*, Nataliya-Mariya ANTONYSHYN[1], Roman GLADYSHEVSKII[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. E-mail: oksana.zaremba@lnu.edu.ua*

Received April 1, 2024; accepted July 1, 2024
https://doi.org/10.30970/cma17.0442

The phase diagram of the $CaO–Tb_2O_3$ (Tb_7O_{12})–CoO system was built based on X-ray diffraction of 21 ceramic polycrystalline samples synthesized by a two-stage solid-state reaction method in air. The formation of two four-component oxides was observed. The existence of the $CaTbCoO_4$ phase (structure type La_2CuO_4, Pearson symbol *oS*28, space group *Cmce*, *a* = 0.53021(5), *b* = 1.1778(1), *c* = 0.52331(5) nm, R_B = 0.079) was revealed for the first time, whereas the formation of the $Ca_2TbCo_2O_6$ compound (structure type $Ca_3Co_2O_6$, Pearson symbol *hR*66, space group *R*-3*c*, *a* = 0.9040(1), *c* = 1.0625(2) nm, R_B = 0.146) was confirmed under the experimental conditions. Examination of other $Ca_{0.5}R_{0.5}CoO_3$ samples (*R* = rare-earth element) indicated the absence of perovskite phases in the corresponding systems, but confirmed the formation of $CaRCoO_4$ compounds with the tetragonal K_2NiF_4 (*R* = Pr^{3+}, Nd^{3+}, and Sm^{3+}) or orthorhombic La_2CuO_4 (*R* = Eu^{3+} and Gd^{3+}) structure types.

Oxides / Solid-state synthesis / X-ray diffraction / Phase diagram / Crystal structure

Introduction

Systems containing alkali-earth (*A*), rare-earth (*R*), 3*d*-transition (*T*) metals and oxygen have attracted the attention of researchers in various fields of science for a long time. This is primarily due to the formation of compounds with perovskite-type structures, which display a number of interesting properties for practical applications. According to literature data, isothermal cross-sections have already been constructed for the Ca–*R*–Co–O systems with *R* = La [1], Nd [2], Sm [3], Eu [4], Gd [5], and Ho [6] at 885°C, and for the Ca–*R*–Co–O systems with *R* = La and Sm [7] at 1100°C. Four-component phases have been reported in all of the Ca–*R*–Co–O systems, except those with *R* = Ce, Pm, and Tm [8]. The major part of the compounds adopts $GdFeO_3$-, K_2NiF_4-, La_2CuO_4-, or $Ca_3Co_2O_6$-type structures. In this work we have performed a systematic study of the Ca–Tb–Co–O system.

Experimental details and results

A two-stage solid-state reaction method was applied for the synthesis of polycrystalline samples in the Ca–Tb–Co–O system and samples of composition $Ca_{0.5}R_{0.5}CoO_3$ (*R* = Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu) in related systems, starting from $CaCO_3$, $CoCO_3$ and rare-earth metal oxide powders of high purity. At first the reagents were mixed, manually ground for 5 minutes after adding each component, and heated in a muffle furnace at 1000°C for 24 h in air. The resulting mixtures were ground, pressed into pellets and annealed in a tube furnace at 1200°C for 8 h in air. Phase and structural analyses were performed using X-ray powder diffraction (XRPD) data collected on a DRON-2.0 M diffractometer (Bragg-Brentano geometry, Fe *Kα* radiation, $20° \leq 2\theta \leq 80°$). The structure refinement (including cell parameters, atomic coordinates, site occupancies) was done by the Rietveld method, applying the DBWS program [9]. To evaluate the correctness of the selected models, the reliability factor R_B was used.

Discussion

Examination of $Ca_{0.5}R_{0.5}CoO_3$ samples, where R = rare-earth metal

Knowledge about the interaction of the components in *A*–*R*–*T*–O systems is widely desired, due to the multiple applications of the compounds, in particular perovskites, which form in them. This prompted us to start the investigation from examining samples with the nominal composition $Ca_{0.5}R_{0.5}CoO_3$ to determine whether perovskite phases form under the experimental conditions. The results of the phase analysis by X-ray diffraction of polycrystalline samples are presented in Table 1. All of the $Ca_{0.5}R_{0.5}CoO_3$ samples were multiphase and did surprisingly not contain any phase with perovskite structure. The samples with Pr and Nd contained in equilibrium $CaPrCoO_4$ / $CaNdCoO_4$ and CoO. The $Ca_{0.5}R_{0.5}CoO_3$ samples, where R = Sm, Eu, Gd, and Tb, turned out to be three-phase, since they contained in addition a four-component phase with the $Ca_3Co_2O_6$ structure type. We have consequently confirmed the existence of ~$CaRCoO_4$ compounds in the systems with Pr, Nd, Sm, Eu, and Gd. According to Thorogood *et al.* [10], for larger ions (Pr^{3+}, Nd^{3+}, and Sm^{3+}), the tetragonal structure type K_2NiF_4 is formed, while for smaller ions (Eu^{3+} and Gd^{3+}) the related orthorhombic structure type La_2CuO_4 is preferred (Table 2). The study of the $Ca_{0.5}Tb_{0.5}CoO_3$ sample revealed a new compound with approximate composition $CaTbCoO_4$, which crystallizes with the La_2CuO_4 structure type.

Table 1 Results of the phase analysis by XRPD of polycrystalline samples of nominal composition $Ca_{0.5}R_{0.5}CoO_3$.

No	Nominal composition	Phase	Structure type	Pearson symbol	Space group	Content, wt.%
1	$Ca_{0.5}Pr_{0.5}CoO_3$	$CaPrCoO_4$ CoO	K_2NiF_4 NaCl	*tI*14 *cF*8	*I4/mmm* *Fm*-3*m*	86.8 13.2
2	$Ca_{0.5}Nd_{0.5}CoO_3$	$CaNdCoO_4$ CoO	K_2NiF_4 NaCl	*tI*14 *cF*8	*I4/mmm* *Fm*-3*m*	82.4 17.6
3	$Ca_{0.5}Sm_{0.5}CoO_3$	$CaSmCoO_4$ CoO $Ca_2SmCo_2O_6$	K_2NiF_4 NaCl $Ca_3Co_2O_6$	*tI*14 *cF*8 *hR*66	*I4/mmm* *Fm*-3*m* *R*-3*c*	64.1 19.6 16.3
4	$Ca_{0.5}Eu_{0.5}CoO_3$	$Ca_2EuCo_2O_6$ $CaEuCoO_4$ CoO	$Ca_3Co_2O_6$ La_2CuO_4 NaCl	*hR*66 *oS*28 *cF*8	*R*-3*c* *Cmce* *Fm*-3*m*	39.5 38.4 22.1
5	$Ca_{0.5}Gd_{0.5}CoO_3$	$CaGdCoO_4$ $Ca_2GdCo_2O_6$ CoO	La_2CuO_4 $Ca_3Co_2O_6$ NaCl	*oS*28 *hR*66 *cF*8	*Cmce* *R*-3*c* *Fm*-3*m*	61.8 21.0 17.2
6	$Ca_{0.5}Tb_{0.5}CoO_3$	$CaTbCoO_4$ $Ca_2TbCo_2O_6$ CoO	La_2CuO_4 $Ca_3Co_2O_6$ NaCl	*oS*28 *hR*66 *cF*8	*Cmce* *R*-3*c* *Fm*-3*m*	60.3 23.0 16.7
7	$Ca_{0.5}Dy_{0.5}CoO_3$	$Ca_2DyCo_2O_6$ Dy_2O_3 CoO	$Ca_3Co_2O_6$ $(Mn_{0.5}Fe_{0.5})_2O_3$ NaCl	*hR*66 *cI*80 *cF*8	*R*-3*c* *Ia*-3 *Fm*-3*m*	62.0 23.0 15.0
8	$Ca_{0.5}Ho_{0.5}CoO_3$	$Ca_2HoCo_2O_6$ Ho_2O_3 CoO	$Ca_3Co_2O_6$ $(Mn_{0.5}Fe_{0.5})_2O_3$ NaCl	*hR*66 *cI*80 *cF*8	*R*-3*c* *Ia*-3 *Fm*-3*m*	61.9 23.6 14.5
9	$Ca_{0.5}Er_{0.5}CoO_3$	$Ca_2ErCo_2O_6$ Er_2O_3 CoO	$Ca_3Co_2O_6$ $(Mn_{0.5}Fe_{0.5})_2O_3$ NaCl	*hR*66 *cI*80 *cF*8	*R*-3*c* *Ia*-3 *Fm*-3*m*	60.9 20.0 19.1
10	$Ca_{0.5}Tm_{0.5}CoO_3$	$Ca_2TmCo_2O_6$ Tm_2O_3 CoO	$Ca_3Co_2O_6$ $(Mn_{0.5}Fe_{0.5})_2O_3$ NaCl	*hR*66 *cI*80 *cF*8	*R*-3*c* *Ia*-3 *Fm*-3*m*	39.5 36.1 24.4
11	$Ca_{0.5}Yb_{0.5}CoO_3$	Yb_2O_3 $Ca_2YbCo_2O_6$ CoO	$(Mn_{0.5}Fe_{0.5})_2O_3$ $Ca_3Co_2O_6$ NaCl	*cI*80 *hR*66 *cF*8	*Ia*-3 *R*-3*c* *Fm*-3*m*	42.9 32.2 24.9
12	$Ca_{0.5}Lu_{0.5}CoO_3$	Lu_2O_3 CoO $Ca_2LuCo_2O_6$	$(Mn_{0.5}Fe_{0.5})_2O_3$ NaCl $Ca_3Co_2O_6$	*cI*80 *cF*8 *hR*66	*Ia*-3 *Fm*-3*m* *R*-3*c*	54.6 29.7 15.7

Table 2 Refined composition and cell parameters of $CaRCoO_4$ phases from XRPD of $Ca_{0.5}R_{0.5}CoO_3$ samples.

No	Refined composition	Structure type	*a*, nm	*b*, nm	*c*, nm	R_B
1	$Ca_{0.84(2)}Pr_{1.16(2)}CoO_4$	K_2NiF_4	0.37537(5)	–	1.1984(2)	0.101
2	$Ca_{0.98(2)}Nd_{1.02(2)}CoO_4$	K_2NiF_4	0.37434(5)	–	1.1937(2)	0.106
3	$Ca_{0.90(1)}Sm_{1.10(1)}CoO_4$	K_2NiF_4	0.37304(3)	–	1.1857(1)	0.137
4	$Ca_{0.90(1)}Eu_{1.10(1)}CoO_4$	La_2CuO_4	0.52802(5)	1.1833(1)	0.52493(5)	0.058
5	$Ca_{0.82(1)}Gd_{1.18(1)}CoO_4$	La_2CuO_4	0.52371(5)	1.1760(1)	0.53028(5)	0.143
6	$Ca_{0.84(1)}Tb_{1.16(1)}CoO_4$	La_2CuO_4	0.53021(5)	1.1778(1)	0.52331(5)	0.079

There is a regular decrease in the volume of the unit cell of the phases with the approximate composition $CaRCoO_4$ when going from Pr to Tb, both for the compounds with K_2NiF_4- and La_2CuO_4-type structures (Fig. 1), that is associated with a gradual decrease of the radii of the rare-earth elements with increasing atomic number [11]. The $Ca_{0.5}R_{0.5}CoO_3$ samples, where R = Dy, Ho, Er, Tm, Yb, and Lu, were also three-phase, but did not contain any phase with 1:1:1:4 stoichiometry. Instead, the diffraction diagrams showed the presence of solid solutions based on the $Ca_3Co_2O_6$ phase, CoO and the corresponding R_2O_3 oxide.

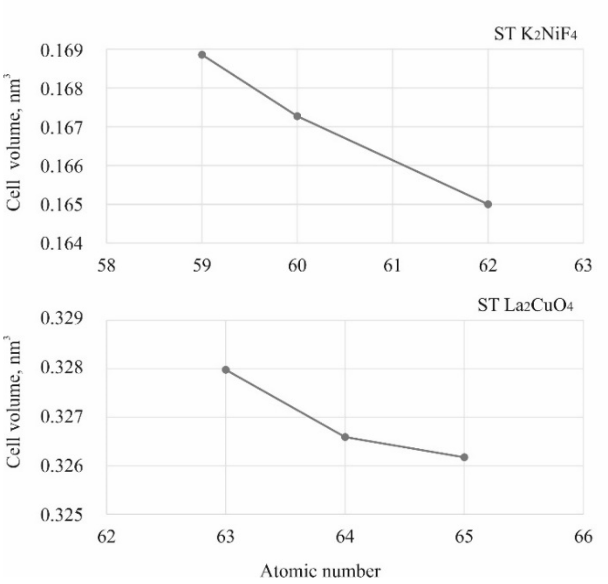

Fig. 1 Cell volume of $CaRCoO_4$ phases *versus* atomic number of the rare-earth metal.

The system $CaO–Tb_2O_3(Tb_7O_{12})–CoO$

The interaction of the components in the $CaO–Tb_2O_3(Tb_7O_{12})–CoO$ system was studied based on X-ray diffraction of 21 polycrystalline samples (Table 3). It should be noted that the initial Tb_2O_3 reagent (structure type $(Mn_{0.5}Fe_{0.5})_2O_3$, Pearson symbol *cI*80, space group *Ia*-3) was, after the synthesis, observed in the form of Tb_7O_{12} (structure type Pr_7O_{12}, Pearson symbol *hR*57, space group *R*-3). This phase dissolves a significant amount of CaO. Fig. 2 shows the phase diagram of the $CaO–Tb_2O_3(Tb_7O_{12})–CoO$ system. There are 5 single-phase, 9 two-phase, and 5 three-phase regions under the conditions of our study. According to Pearson's Crystal Data [8], several compounds have been reported in the Tb_2O_3–CoO and CaO–CoO boundary systems (including the compound $Ca_3Co_2O_6$), while there are no data on the formation of compounds in the system $CaO–Tb_2O_3$. Under the conditions of our experiment, no compound was observed in any of the boundary systems. The existence of the compound $Ca_2TbCo_2O_6$ (ST $Ca_3Co_2O_6$), with point composition, was confirmed. It is in equilibrium with the phases $CaTbCoO_4$, CoO, CaO, and the solid solution of CaO in terbium oxide. The existence of the phase of approximate composition $CaTbCoO_4$ (structure type La_2CuO_4), observed in the $Ca_{0.5}Tb_{0.5}CoO_3$ sample, was confirmed. This phase is in equilibrium with CoO, $Ca_2TbCo_2O_6$, and the solid solution based on terbium oxide. The results of the crystal structure refinements of the two four-component phases are shown in Table 4 and Table 5. Despite the fact that the compound $CaTbCoO_4$ has orthorhombic, and $Ca_2TbCo_2O_6$ hexagonal symmetry, both structures are characterized by the same coordination environment of the Co atoms, which are surrounded by 6 oxygen atoms forming an octahedron (Fig. 3).

Summary

A systematic investigation of the Ca–*R*–Co–O systems, revealed that they do not contain four-component perovskite phases under ordinary experimental conditions. Instead, the existence of $CaRCoO_4$ compounds with R = Pr, Nd, Sm, Eu, and Gd was confirmed, and a new compound, $CaTbCoO_4$, was discovered with a La_2CuO_4-type structure. The phase equilibria in the $CaO–Tb_2O_3(Tb_7O_{12})–CoO$ system were constructed, confirming the existence of the $Ca_2TbCo_2O_6$ compound, in addition to the previously unreported $CaTbCoO_4$ phase. These findings add to our understanding of complex oxide systems with potential prospects for practical applications.

Table 3 Results of the phase analysis by XRPD of polycrystalline samples of the $CaO–Tb_2O_3–CoO$ system.

No	Nominal composition	Phase	Structure type	Pearson symbol	Space group	Content, wt.%
1	$CaO-CoO$ (60:40 mol.%)	CaO	$NaCl$	*cF*8	*Fm*-3*m*	58.6
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	41.4
2	$CaO-1/2Tb_2O_3-CoO$ (55:5:40 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	42.8
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	31.0
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	26.2
3	$CaO-1/2Tb_2O_3-CoO$ (40:5:55 mol.%)	CoO	$NaCl$	*cF*8	*Fm*-3*m*	43.0
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	38.4
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	18.6
4	$CaO-1/2Tb_2O_3-CoO$ (50:10:40 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	70.7
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	17.5
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	11.8
5	$CaO-1/2Tb_2O_3-CoO$ (45:15:40 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	100
6	$CaO-1/2Tb_2O_3-CoO$ (25:25:50 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	60.3
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	23.0
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	16.7
7	$CaO-1/2Tb_2O_3-CoO$ (60:10:30 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	65.8
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	27.6
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	6.6
8	$CaO-1/2Tb_2O_3$ (10:90 mol.%)	Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	100
9	$CaO-1/2Tb_2O_3$ (20:80 mol.%)	Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	94.7
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	5.3
10	$CaO-1/2Tb_2O_3$ (30:70 mol.%)	Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	87.6
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	12.4
11	$CaO-1/2Tb_2O_3$ (40:60 mol.%)	Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	84.8
		CaO	$NaCl$	*cF*8	*Fm*-3*m*	15.2
12	$CaO-1/2Tb_2O_3-CoO$ (40.0: 26.7:33.3 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	54.9
		$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	38.0
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	7.1
13	$CaO-1/2Tb_2O_3-CoO$ (33.4:33.3:33.3 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	62.7
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	30.4
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	6.9
14	$CaO-1/2Tb_2O_3-CoO$ (30.0: 36.7:33.3 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	79.0
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	17.9
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	3.1
15	$CaO-1/2Tb_2O_3-CoO$ (26.7:40:33.3 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	90.7
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	9.3
16	$CaO-1/2Tb_2O_3-CoO$ (20: 46.7:33.3 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	60.9
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	30.1
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	9.0
17	$CaO-1/2Tb_2O_3-CoO$ (30:20:50 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	67.9
		$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	19.0
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	13.1
18	$CaO-1/2Tb_2O_3-CoO$ (40:20:40 mol.%)	$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	95.1
		$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	3.5
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	1.4
19	$CaO-1/2Tb_2O_3-CoO$ (10:50:40 mol.%)	Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	57.2
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	24.2
		$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	18.6
20	$CaO-1/2Tb_2O_3-CoO$ (25:50:25 mol.%)	$CaTbCoO_4$	La_2CuO_4	*oS*28	*Cmce*	50.9
		Tb_7O_{12}	Pr_7O_{12}	*hR*57	*R*-3	36.5
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	12.6
21	$CaO-1/2Tb_2O_3-CoO$ (60:5:35 mol.%)	CaO	$NaCl$	*cF*8	*Fm*-3*m*	42.8
		$Ca_2TbCo_2O_6$	$Ca_3Co_2O_6$	*hR*66	*R*-3*c*	35.5
		CoO	$NaCl$	*cF*8	*Fm*-3*m*	21.7

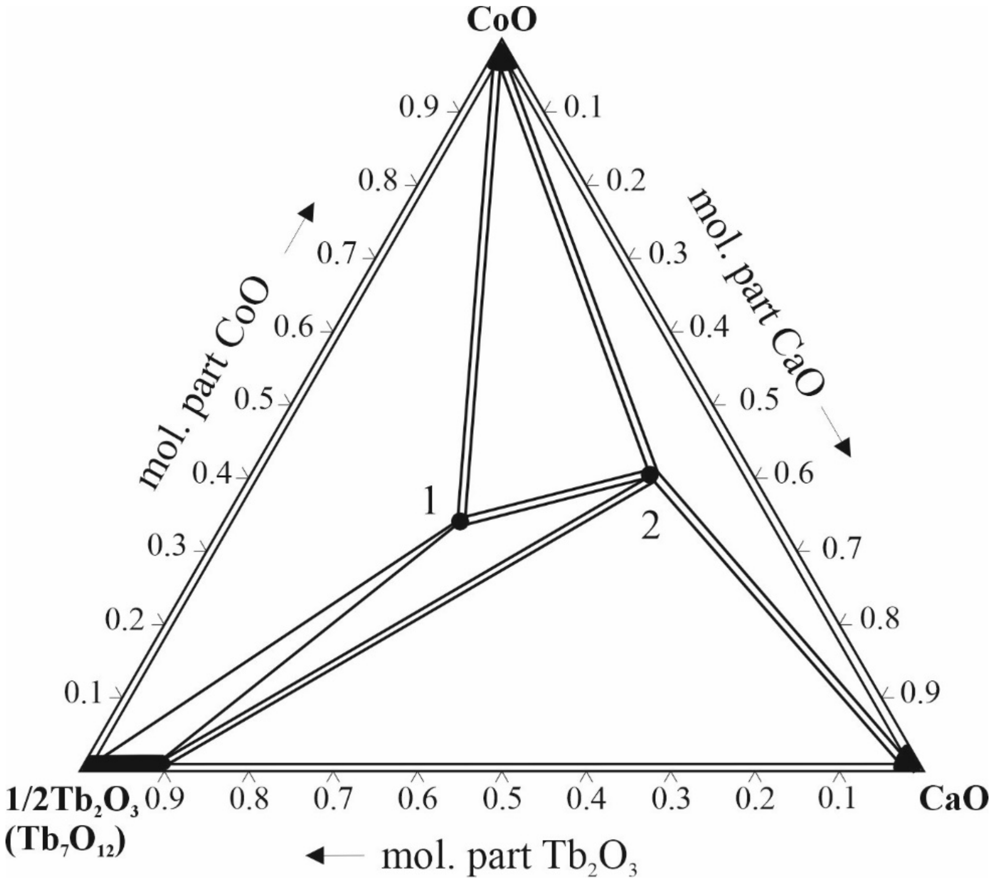

Fig. 2 Phase diagram of the CaO–Tb_2O_3(Tb_7O_{12})–CoO system (1 – $CaTbCoO_4$, 2 – $Ca_2TbCo_2O_6$).

Table 4 Atomic coordinates of $CaTbCoO_4$ from XRPD (ST La_2CuO_4, PS *oS*28, SG *Cmce*, *a* = 0.53021(5), *b* = 1.1778(1), *c* = 0.52331(5) nm, R_B = 0.079).

Atom	Wyckoff position	Atomic coordinates		
		x	*y*	*z*
O1	8*e*	¼	0.001	¼
0.42(1)Ca + 0.58(1)Tb	8*f*	0	0.359(1)	0.008(2)
O2	8*f*	0	0.333	0.493
Co	4*a*	0	0	0

Table 5 Atom coordinates of $Ca_2TbCo_2O_6$ from XRPD (ST $Ca_3Co_2O_6$, PS *hR*66, SG *R*-3*c*, *a* = 0.9040(1), *c* = 1.0625(2) nm, R_B = 0.146).

Atom	Wyckoff position	Atomic coordinates		
		x	*y*	*z*
O	36*f*	0.1766	0.0244	0.1138
0.69(1)Ca + 0.31(1)Tb	18*e*	0.3688(5)	0	¼
Co1	6*b*	0	0	0
Co2	6*a*	0	0	¼

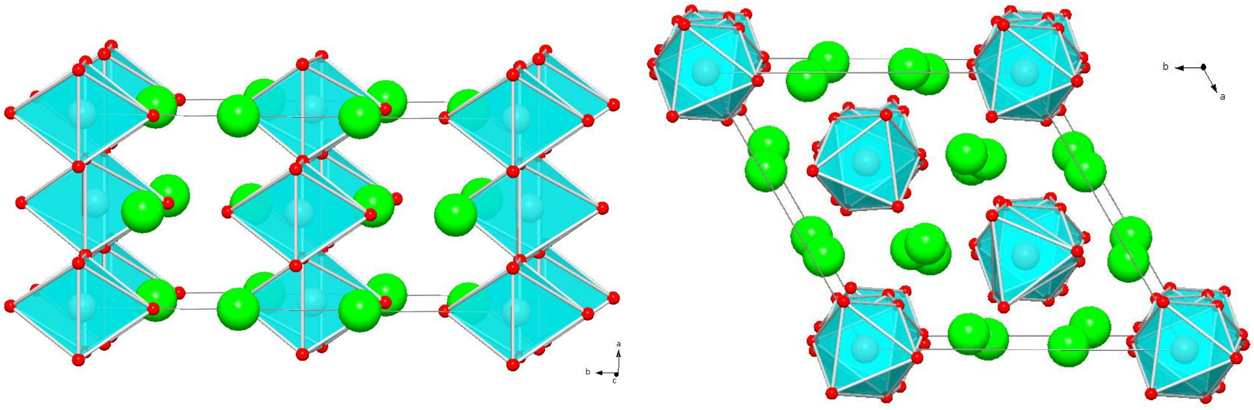

Fig. 3 Arrangement of CoO_6 octahedra in $CaTbCoO_4$ (left) and $Ca_2TbCo_2O_6$ (right).

Acknowledgments

OZ is grateful to the Simons Foundation (award No. 1290588) for partial financial support.

References

[1] W. Wong-Ng, W.J. Laws, Y.G. Yan, *Solid State Sci*. 13 (2013) 107-110. https://doi.org/10.1016/j.solidstatesciences.2012.11.021

[2] 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. https://doi.org/10.1016/j.jssc.2014.03.012

[3] W. Wong-Ng, W. Laws, S.H. Lapidus, J.A. Kaduk, *Solid State Sci*. 48 (2015) 31-38. https://doi.org/10.1016/j.solidstatesciences.2015.06.003

[4] W. Wong-Ng, W. Laws, J.A. Kaduk, *Solid State Sci*. 58 (2016) 105-110. https://doi.org/10.1016/j.solidstatesciences.2016.06.007

[5] W. Wong-Ng, W. Laws, S.H. Lapidus, L. Ribaud, J.A. Kaduk, *Solid State Sci*. 72 (2017) 47-54. https://doi.org/10.1016/j.solidstatesciences.2017.08.005

[6] W. Wong-Ng, W. Laws, Q. Huang, J. Hou, S.H. Lapidus, L. Ribaud, J.A. Kaduk, *Solid State Sci*.107 (2020) 106348. https://doi.org/10.1016/j.solidstatesciences.2020.106348

[7] *Phase Equilibria Diagrams Database*, ACS and NIST, Westerville, OH, USA.

[8] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA.

[9] D.B. Wiles, A. Sakthivel, R.A. Young, *Program DBWS3.2 for Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns*, School of Physics, Georgia Institute of Technology, Atlanta, 1998.

[10] G.J. Thorogood, P.-Y. Orain, M. Ouvry, B. Piriou, T. Tedesco, K.S. Wallwork, J. Herrmann, M. James, *Solid State Sci*. 13 (2011) 2113-2123. https://doi.org/10.1016/j.solidstatesciences.2011.08.008

[11] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751-767. https://doi.org/10.1107/S0567739476001551