

Interaction of the Components in the BaO–Tb₂O_{3+δ}–CuO and Related Systems

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The isothermal section of the phase diagram of the BaO–Tb₂O_{3+δ}–CuO system at 1173 K was constructed based on X-ray powder diffraction data. The existence of the compounds BaTbO₃ (SrZrO₃ structure type, *I4/mcm*, $a = 0.6034(1)$, $c = 0.8576(1)$ nm) and Ba₄₄Cu₄₅O₉₀ (own structure type, *Im-3m*, $a = 1.8266(3)$ nm) was confirmed in the binary BaO–Tb₂O₃ and BaO–CuO systems, respectively, but no ternary oxides were found. The investigation of samples with nominal composition A_{0.5}Tb_{0.5}TO₃ (A = Ca, Sr or Ba, T = Ni or Zn) showed the presence of phases from the corresponding binary systems, or unreacted reagents.

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1. Introduction

The A–R–Cu–O systems, where A is an alkaline-earth and R is a rare-earth metal, have attracted considerable interest for a long time. The compounds in these systems are usually characterized by layered structures, and are first of all interesting as high-temperature superconductors. The most prominent among them is undoubtedly YBa₂Cu₃O₇ (YBCO), the crystal structure and properties of which have been meticulously studied. The interaction of the components in the system Ba–Y–Cu–O and related systems with other alkaline-earth and rare-earth metals has also been extensively investigated [1]. In this work we focus on the system Ba–Tb–Cu–O and some related systems with Tb, for which data in the literature are scarce.

2. Experimental

Polycrystalline samples of the BaO–Tb₂O_{3+δ}–CuO system were prepared by solid-state reaction of appropriate amounts of high-purity carbonates and oxides at 1173 K in air in two 24 h stages. Firstly, the reagents were mixed and heated in a corundum crucible to decompose the carbonates. Then, after cooling to room temperature, the mixtures were reground to achieve homogeneity, pressed into pellets and sintered. Samples of nominal composition A_{0.5}Tb_{0.5}TO₃, where A = Ca, Sr or Ba, T = Ni or Zn, were prepared in a similar way. Phase and structure analyses were carried out on X-ray powder diffraction data (DRON 2.0M diffractometer, Fe K_α radiation, DBWS program [2]).

3. Results and discussions

The isothermal section of the phase diagram of the BaO–Tb₂O_{3+δ}–CuO system at 1173 K was constructed based on the investigation of 15 samples. Table I (at the end) contains the results of the phase analysis of some of

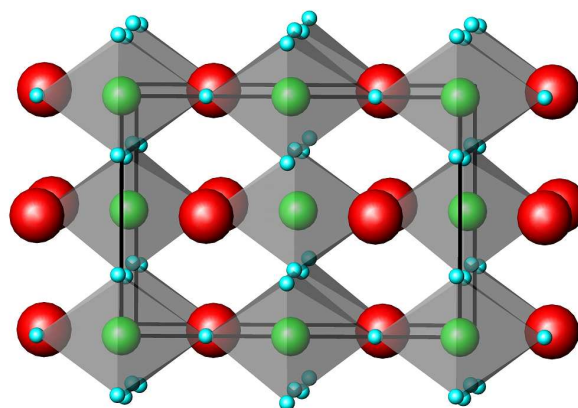


Fig. 1. Crystal structure of BaTbO₃ (the coordination polyhedra of the Tb atoms are shown as shaded octahedra [O₆]).

TABLE II

Number of quaternary compounds formed in Ba–R–Cu–O systems, where R is a rare-earth metal [1].

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
14	1	5	9	-	9	7	8
Y	Tb	Dy	Ho	Er	Tm	Yb	Lu
13	1	6	8	6	5	8	3

the samples. The existence of the compounds BaTbO₃ (SrZrO₃ structure type, *I4/mcm*, $a = 0.6034(1)$, $c = 0.8576(1)$ nm, $R_B = 0.052$) and Ba₄₄Cu₄₅O₉₀ (own structure type, *Im-3m*, $a = 1.8266(3)$ nm, $R_B = 0.183$) was confirmed in the binary BaO–Tb₂O₃ and BaO–CuO boundary systems. The former adopts a tetragonal perovskite structure (Fig. 1), whereas the large cubic unit cell of the latter contains some 400 atoms. It was found that the interaction of the components in the ternary region of the BaO–Tb₂O_{3+δ}–CuO system is characterized by the absence of compounds. The only compound reported in the literature, TbBa₂Cu₃O₇ with orthorhombic YBa₂Cu₃O₇ structure type [3], was consequently

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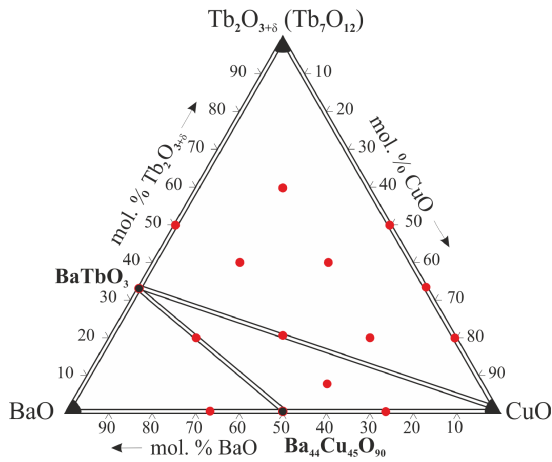


Fig. 2. Isothermal section of the phase diagram of the BaO–Tb₂O_{3+δ}–CuO system at 1173 K (the samples used for the investigation are indicated as circles).

TABLE III

Results of the phase analysis of samples with nominal composition A_{0.5}Tb_{0.5}TO₃, where A = Ca, Sr or Ba, T = Ni or Zn.

Nominal composition	Phase	Structure type	Pearson symbol	Space group	Phase content [wt%]
Ba _{0.5} Tb _{0.5} ZnO ₃	BaTbO ₃	SrZrO ₃	<i>tI</i> 20	<i>I4/mcm</i>	59.9
	ZnO	ZnO	<i>hP</i> 4	<i>P6₃mc</i>	40.1
Sr _{0.5} Tb _{0.5} ZnO ₃	SrTbO ₃	GdFeO ₃	<i>oP</i> 20	<i>Pnma</i>	71.9
	ZnO	ZnO	<i>hP</i> 4	<i>P6₃mc</i>	28.1
Ca _{0.5} Tb _{0.5} ZnO ₃	ZnO	ZnO	<i>hP</i> 4	<i>P6₃mc</i>	43.0
	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR</i> 57	<i>R-3</i>	42.0
	CaO	NaCl	<i>cF</i> 8	<i>Pm-3m</i>	15.0
Ca _{0.5} Tb _{0.5} NiO ₃	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR</i> 57	<i>R-3</i>	42.9
	NiO	NaCl	<i>cF</i> 8	<i>Pm-3m</i>	41.1
	CaO	NaCl	<i>cF</i> 8	<i>Pm-3m</i>	16.0

not observed under the conditions of our study. The BaTbO₃ phase is in equilibrium with the Ba₄₄Cu₄₅O₉₀ and CuO phases. Hence, there are three three-phase and two two-phase regions in the system (Fig. 2). It should be

noted that, during the synthesis, the initial cubic Tb₂O₃ phase with (Mn_{0.5}Fe_{0.5})₂O₃-type structure was oxidized into the rhombohedral Tb₇O₁₂ phase with Pr₇O₁₂-type structure.

Among the systems Ba–R–Cu–O, where R is a rare-earth metal, the lowest numbers of compounds (Table II) have been reported in the systems with Ce (only CeBa₂Cu₃O_{7.4} [4]) and Tb (only TbBa₂Cu₃O₇ [3]). Presumably this is connected with the possibility of these R elements to adopt oxidation states higher than 3+. Our investigation confirmed that the interaction of the components in the system Ba–Tb–Cu–O does not lead to the formation of a high number of compounds, as is the case for some related systems.

Among the selected samples from related systems with Tb (Table III), Ba_{0.5}Tb_{0.5}ZnO₃ and Sr_{0.5}Tb_{0.5}ZnO₃ were found to be two-phase samples, containing in equilibrium BaTbO₃ (SrZrO₃ structure type, *I4/mcm*, *a* = 0.6039(1), *c* = 0.8578(1) nm, *R_B* = 0.099), or SrTbO₃ (GdFeO₃ structure type, *Pnma*, *a* = 0.5945(1), *b* = 0.8347(2), *c* = 0.5879(1) nm, *R_B* = 0.160), and ZnO. The investigation of the samples with nominal compositions Ca_{0.5}Tb_{0.5}ZnO₃ and Ca_{0.5}Tb_{0.5}NiO₃ showed the presence of the initial compounds CaO, Tb₇O₁₂ and ZnO (or NiO) in the expected ratios. Consequently, it can be concluded that the intensity of the interaction of the components decreases on going from the Ba- to the Ca-containing system.

References

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TABLE I

Results of the phase analysis of the quaternary samples used for the investigation of the BaO–Tb₂O_{3+δ}–CuO system.

Nominal composition of the sample BaO:Tb ₂ O ₃ :CuO [mol.%]	Phase	Structure type	Pearson symbol	Space group	Phase content [wt%]
36.4:9.1:54.5	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	55.8
	Ba ₄₄ Cu ₄₅ O ₉₀	Ba ₄₄ Cu ₄₅ O ₉₀	<i>cI400</i>	<i>Im-3m</i>	25.9
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	18.3
60:20:20	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	77.1
	Ba ₄₄ Cu ₄₅ O ₉₀	Ba ₄₄ Cu ₄₅ O ₉₀	<i>cI400</i>	<i>Im-3m</i>	22.9
40:20:40	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	77.9
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	22.1
20:20:60	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	42.6
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	36.1
	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR57</i>	<i>R-3</i>	21.3
40:40:20	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	63.2
	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR57</i>	<i>R-3</i>	28.1
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	8.7
20:40:40	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR57</i>	<i>R-3</i>	49.9
	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	33.9
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	16.2
20:60:20	Tb ₇ O ₁₂	Pr ₇ O ₁₂	<i>hR57</i>	<i>R-3</i>	58.0
	BaTbO ₃	SrZrO ₃	<i>tI20</i>	<i>I4/mcm</i>	35.2
	CuO	CuO	<i>mS8</i>	<i>C2/c</i>	6.8