Subsolidus phase relationships of the BaO–R₂O₃–CuOₓ \( (R = \text{Gd and Er}) \) systems under carbonate-free conditions at \( p_{O_2} = 100 \) Pa and \( T = 810 \) °C

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Abstract

The phase diagrams of the BaO–Gd₂O₃–CuOₓ and BaO–Er₂O₃–CuOₓ systems were determined at 100 Pa \( (0.1\% \text{ O}_2 \text{ by volume, } 810 \) °C) by using special apparatus and a procedure for preparing carbonate-free precursors based on BaO. The diagram of the BaO–Er₂O₃–CuOₓ system was confirmed to be similar to that of the Y-analog. The diagram of the BaO–Gd₂O₃–CuOₓ system exhibits different features as compared to the Er-analog. While the Er-system includes the Er₂Cu₂O₅ phase, the Gd-system involves the Gd₂CuO₄ phase instead. The absence of the Ba₃R₄O₉ phase in the Gd-system affects the tie-line relations in the region bounded by BaO, BaGd₂O₄, BaGd₂CuO₅ and Ba₆GdCu₃O₁₆. In general, both the diagrams of the BaO–Er₂O₃–CuOₓ and of the BaO–Gd₂O₃–CuOₓ systems prepared under carbonate-free conditions are different from those obtained using BaCO₃-derived starting materials. For applications of phase equilibria to coated conductor processing, phase diagrams constructed under carbonate-free conditions should be employed.

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Keywords: Superconductors; Phase equilibria; BaO–R₂O₃–CuOₓ \( (R = \text{Gd and Er}) \); Carbonate-free conditions

1. Introduction

Following the discovery of high \( T_c \) superconducting oxides in 1986 [1], considerable technological progress has been achieved. In the area of wire and tape development, intensive research has led to the powder-in-tube (PIT) process for fabrication of Bi–Pb–Sr–Ca–Cu–O (BSCCO) tapes [2–6]. Current research and development efforts in PIT technology, or so-called first-generation wire and tape, are focused on improving processing routes to optimize performance and minimize cost. More recently, second-generation high-\( T_c \) superconductor tapes deposited on flexible coated-conductors have received increasing attention [7–11]. Second-generation superconductors are based on BaO–Y₂O₃–CuO₂ materials [12–14], including lanthanide-substituted variants. The Ba–Y–Cu–O and Ba–R–Cu–O \( (R = \text{lanthanides}) \) materials are relatively more isotropic when compared with BSCCO-based superconductors, and can retain current-carrying ability at liquid nitrogen temperature under high magnetic fields. As a result, coated-conductor superconductors have great commercial potential for electric utility and high magnetic field applications. Three second-generation coated-conductor processes are furthest along in their technological development: the rolling-assisted biaxially textured substrate process (RABiTS) [7,8], and the ion beam-assisted deposition process (IBAD) [9,10], and the inclined substrate deposition (ISD) [11].

The development of coated-conductor superconductors has produced renewed research interest in the entire family of the \( \text{Ba}_2\text{RCu}_3\text{O}_6+z \) materials \( (R = \text{Y and lanthanide elements}) \). Our phase diagram studies of the BaO–R₂O₃–CuO₂ \( (R = \text{Nd} [15], \text{Sm} [16] \text{ and Y} [17]) \) systems under carbonate-free conditions have been designed to match RABiTS and IBAD processing conditions. The goal of the present paper is to extend our studies to the \( R = \text{Gd and Er} \) systems under similar experimental conditions \( (p_{O_2} = 100 \) Pa, \( T = 810 \) °C, BaO as a source for Ba). Various phase diagrams of the
BaO–Er₂O₃–CuO [18–21] and BaO–Gd₂O₃–CuO [18,22–25] systems are available in literature; however, the majority of these diagrams were prepared using BaCO₃ as one of the starting reagents, partly because it is difficult to handle BaO. The crystal chemistry and crystal structure of compounds of the BaO–R₂O₃–CuO₂ systems have been reported extensively and will not be discussed in detail here. Emphasis will be placed on the phase formation and phase compatibilities, which are important for processing.

2. Experimental details

2.1. Preparation of BaO

BaO starting material was produced from BaCO₃ (99.99% purity, metals basis) by vacuum calcination in a specially designed vertical tube furnace. An MgO crucible containing ~ 15 g of BaCO₃ was suspended in the hot zone of the furnace, and the furnace was evacuated to a pressure of ~ 10 µm Hg or less by a high capacity mechanical pump. The following heating schedule was used: room temperature to 1300 °C in 20 h; isothermal at 1300 °C for 10 h; 1300 °C to room temperature in 20 h. During vacuum calcination the pressure typically increased to ~ 200 µm Hg as CO₂ was evolved, and then rapidly returned to ~ 10 µm Hg or less as the decomposition of the BaCO₃ was completed. After cooling, the BaO was lowered through an interlock into a transfer vessel. It was then transported to an Ar-filled glove-box continuously purged with a recirculating purifier, which removed atmospheric contaminants from the Ar to < 1 ppm by volume. Characterization by X-ray powder diffraction showed only the characteristic peaks for BaO.

2.2. Sample preparation

All sample weighings, homogenizations and pressings of pellets were performed inside the glove-box. Pelletized samples were placed inside individual MgO crucibles for annealing in a horizontal box-type controlled-atmosphere furnace. Transfer from the glove-box to the box furnace and vice versa was achieved via a second transfer vessel and an interlock system attached to the furnace.

Samples of forty compositions for the BaO–Er₂O₃–CuO system (Table 1) and thirty three compositions for the BaO–Gd₂O₃–CuO₂ system (Table 2) were prepared using the solid state sintering method. Stoichiometric amounts of BaO, R₂O₃ (R = Gd and Er) (99.99% purity, metals basis), and CuO (99.99% purity, metals basis) were mixed and pressed into pellets, and annealed in the box furnace. During the annealing, the oxygen pressure of Ar/O₂ mixtures was controlled using a mass flow meter and monitored at both the inlet and outlet of the furnace using a zirconia oxygen sensor. Samples were annealed at 810 °C for the experiments at pO₂ = 100 Pa (0.1% O₂ by volume). Intermediate grindings and pelletizings took place until no further changes were detected in the powder X-ray diffraction patterns. Samples were processed for about 3 weeks each. All X-ray patterns were obtained using a hermetic cell designed for air-sensitive materials [26].

2.3. X-ray powder diffraction

For X-ray phase analysis, specimens were loaded into a sealed cell designed by Ritter [26]. The process of sample loading was performed inside an Ar-filled glove box. X-ray

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1 Certain commercial equipment, instruments or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
powder diffraction was used to identify the phases synthesized and to confirm phase purity. Data were collected using a computer-controlled automated diffractometer equipped with a theta-compensation slit. Cu-Kα radiation was used at 45 kV and 40 mA. The radiation was detected by a scintillation counter and a solid-state amplifier. A Siemens diffraction software package and reference X-ray diffraction patterns of the ICDD powder diffraction file (PDF) [27] were used for phase identification.

3. Results and discussion

Figs. 1 and 2 give the phase diagrams of the BaO–Er₂O₃–CuOₓ and the BaO–Gd₂O₃–CuOₓ systems prepared at pO₂ = 100 Pa (≈ 810°C). The diagrams appear to be relatively simple, but are different from those prepared using BaCO₃ [18–21], particularly in the Ba-rich region. There is no detectable solid solution formation of compounds in these systems under the current experimental conditions.

3.1. Phase formation

3.1.1. BaO–Er₂O₃–CuOₓ system

The BaO–CuOₓ system. The reduced phase BaCu₂O₂₊ₓ was observed in addition to Ba₂CuO₃₊ₓ and BaCuO₂₊ₓ. A review of the crystal chemistry and crystallography of the phases in the BaO–CuOₓ system was given by Wong-Ng and Cook [28]. In the BaO–CuOₓ system, the compounds Ba₂CuO₃₊ₓ [29–32] and BaCuO₂₊ₓ were found to be stable at pO₂ = 100 Pa. The Ba₂CuO₃₊ₓ phase is atmospherically very sensitive, and cannot be prepared in the presence of moisture and carbonate. The oxygen content of the BaCuO₂₊ₓ series has been reported to vary between 2.0 and 2.5. Three structure types are known (0 < z < 0.12, 0.29 < z < 0.36 and z = 0.5). The most commonly recognized structure form is cubic, with 0 < z < 0.12. Phase compositions with z greater than 0.12 have been reported by Petricek et al. [33]. There is no evidence for the existence of the Ba₂Cu₃O₅₊ₓ or Ba₃Cu₅O₉₊ₓ phases [28]. The Ba₃CuO₄ phase, reported by Frase and Clarke [34] and Abbattista et al. [35,36] to be stable under very reduced conditions, was not detected in the present study. As the ionic sizes of Ba and Er [37] are rather different [1.52 Å (X-coordination for Ba²⁺) vs. 0.890 Å for Er³⁺], no solid solution of the (Ba,Er)₂CuO₃₊ₓ type was observed, in contrast to the BaO–Nd₂O₃–CuOₓ [15] and the BaO–Sm₂O₃–CuOₓ systems [16].

BaO–Er₂O₃. In the BaO–Er₂O₃ system, Ba₃Er₂O₉ and Ba₂Er₂O₅ [17] were found at pO₂ = 100 Pa. The Er analogs of the Ba₂R₂O₅ and Ba₄R₂O₉ types reported in the BaO–Y₂O₃–CuOₓ system prepared with BaCO₃-derived starting materials [38] are not stable here. These phases have been determined by Abbattista et al. [36] and DeLeeuw et al. [39] to correspond to Ba₂Y₂O₅·CO₂ and Ba₄Y₂O₉·2CO₂.

Er₂O₃–CuOₓ. In the binary Er₂O₃–CuOₓ diagrams, only the Er₂Cu₂O₅ phase was observed at pO₂ = 21 kPa [40]. The R₂CuO₄-type phase only exists when R is relatively large (lanthanides with ionic radius r > rDy³⁺). As the ionic radius of R³⁺ decreases beyond Gd (from Dy to Lu), the R₂Cu₂O₅-type phase (orthorhombic, Pbca) was found instead of R₂CuO₄ [13]. The reported reduced phase of the YCuO₂ structure type [41,42] was not found; presumably the oxygen partial pressure of pO₂ = 100 Pa is not sufficiently low to stabilize this phase.
BaO–Er₂O₃–CuO₉. A total of four ternary oxides (Ba₃ErCu₃O₉₊ₓ; 2:1:3), Ba₂ErCu₅O₁₀ (4:1:3), Ba₃ErCu₅O₁₀ (6:1:3), and the ‘green phase’ Ba₄Er₃Cu₉O₁₅ (1:2:1) was found in the BaO–Er₂O₃–CuO₉ system. The occurrence of the compounds Ba₂ErCu₅O₁₀ and Ba₆Er₃Cu₅O₁₅ in the BaO-rich part of the diagram is similar to that of the BaO–Y₂O₃–CuO₉ system [17,35,43]. The structure of Ba₁₂Er₆Cu₉O₃₁ was reported to be of the cubic oxygen-defect perovskite type (a = 8.08236(5) Å when prepared in oxygen) [44]. The orthorhombic Ba₂Er₃Cu₅O₁₀ phase is of the SrTiO₃-type (layered perovskite structure) [45]. The structure of the BaEr₂Cu₅O₉ “green” phase, orthorhombic with space group Pnma, has been studied extensively [46–48].

Similar to Ba₂YCu₃O₆₊ₓ, the Ba₂Er₃Cu₅O₆₊ₓ (2:1:3) phase is a stoichiometric compound with respect to the cation content. By contrast, solid solution was reported in the lanthanide-containing Ba₂−ₓRₓ₊₁Cu₃O₆₊ₓ phases with relatively larger size of R (for example, R = Nd and Sm) when samples were also prepared under 100 Pa [15,16]. The Shannon ionic radius of Ba (1.52 Å (X-coordination [37])) and R are more comparable for lighter lanthanides (0.958 to 1.032 Å from Sm to La, VIII-coordination).

3.1.2. BaO–Gd₂O₃–CuO₉ system

The phases found in the BaO–CuO₉ system are the same as those in the Er-system, namely, Ba₂Cu₃O₆₊ₓ, BaCuO₂+x, and BaCu₂O₂+x. BaO–Gd₂O₃. The BaGd₂O₄ phase was the only compound found in the binary BaO–Gd₂O₃ system. BaGd₂O₄ was reported to crystallize in the orthorhombic Pnma system [49], which is isostructural with the BaNd₂O₄ structure [50]. The Ba₃R₄O₉-type phase (rhombohedral R3m) which exists in systems with smaller R³⁺ (for example, R = Ho, Y, Er, etc.) [51] cannot be prepared with the relatively larger Gd³⁺. Similar to the Er-analog, the Ba₂R₂O₆ and Ba₂R₂O₇ phases reported in systems when BaCO₃ was used as a starting reagent were also found to be absent under carbonate-free conditions.

Gd₂O₃–CuO₉. In the Gd₂O₃–CuO₉ system, Gd₂CuO₄ (tetragonal I4/mmm symmetry [52]) was confirmed to be the only compound formed. Apparently under 100 Pa O₂, the reduced rhombohedral RCuO₂+ phase was reported by Refs. [41,42] is not stable. Luce and Stacy [30] reported an oxidized monoclinic phase of RCuO₂ (12/a, a = 5.7813(3) Å, b = 9.6581(5) Å, c = 5.7062(3) Å, β = 92.305(2)°). However, this phase is not expected to be stable under reducing conditions.

BaO–Gd₂O₃–CuO₉. There are a total of three ternary oxide phases in the ternary BaO–Gd₂O₃–CuO₉ system. No solid solution was found in this system. These four phases are Ba₂GdCu₃O₆₊ₓ, Ba₆GdCu₃O₆, and Ba₆GdCu₅O₉. The Gd-613 phase was reported by Osamura and Zhang [45] to be perovskite-related phase. However, unlike the Er-613 phase which was reported to be orthorhombic, the Gd-613 was reported to be tetragonal (I4/mmm, a = 4.074(4) Å and c = 21.696 Å when prepared in air). While the Ba₂GdCu₃O₉ phase [53] can be prepared under O₂ condition, it cannot be prepared under reduced 100 Pa O₂. Under 100 Pa O₂, the ‘green phase’ BaGd₂Cu₃O₉ is isostructural to BaEr₂Cu₅O₁₅, but has a different structure from that of the Nd–brown phase, BaNd₂Cu₃O₆ (Nd-121). While Nd-121 is tetragonal I4/mmm, Gd-121 is orthorhombic Pbnm [48].

3.2. Phase compatibilities

3.2.1. BaO–Er₂O₃–CuO₉

The tie-lines determined near the CuO₂ and Er₂O₃ regions are in agreement with most other diagrams, whether prepared using BaCO₃, Ba₂O₃, Ba₂O₃ or Ba(NO₃)₂. However, the diagram near BaO region is substantially different. This diagram is similar to that of the BaO–Y₂O₃–CuO₉ system reported by us [17]. The tie-line relationships around the 213 phase which involve the four phases, Ba₂ErCu₃O₆₊ₓ, BaEr₂CuO₄, BaCuO₂+x, and Ba₆ErCu₃O₉, are also different from the literature data. For example, in the present study, the Ba₂Er₃Cu₅O₁₅ phase is found to be compatible to the Ba₄ErCu₃O₁₅ phase, whereas most literature phase diagrams reported today involve a tie-line between Ba₂CuO₂+x and Ba₂CuO₃ [18–22,24,25,54–56]. The formation of the tie-line between Ba₂RCu₃O₆₊ₓ and Ba₄RCu₃O₉ was also found in our previous studies of the Nd-, Sm- and Y-systems [15–17], and during the investigation of the melting equilibria of the BaO-Y₂O₃-CuO₂ system [57]. The majority of literature studies were not conducted entirely under atmospherically-controlled conditions, and it is clear that the presence of CO₂ affects the tie-line relationships.

3.2.2. BaO–Gd₂O₃–CuO₉

The tie-line distribution in the BaO–Gd₂O₃–CuO₉ system, as shown in Fig. 2, is in general similar to that found in the BaO–Sm₂O₃–CuO₉ system [16]. Due to the greater mismatch of the Ba²⁺ and Gd³⁺ (1.52 vs. 0.938 Å) as compared with the Ba²⁺ and Sm³⁺ (1.52 vs. 0.958 Å), while there is a single phase range of the ternary solid solutions Ba₂+xSm₁−ₓCu₁O₆+x (0 ≤ x ≤ 0.2), in the BaO–Sm₂O₃–CuO₉ system, the Gd-213 phase is a stoichiometric compound. As a result, there is no tie-line bundle connecting the Gd-213 phase to the ‘green phase’, BaGd₂Cu₃O₉, and to the CuO₂ phase. The absence of the Ba₃R₂O₆ phase, as compared to the Er-system, affects the tie-line relations in the region bounded by BaO, BaGd₂O₄, Ba₆GdCu₃O₉, and Ba₁₂GdCu₁₅O₃₁. All ternary oxides are compatible with at least five other phases. In the case of BaGd₂Cu₃O₉, seven tie-lines were found to originate from it. In the BaO-rich region, tie-lines are found between BaO and BaGd₂Cu₃O₉, and between BaO and Ba₆GdCu₅O₉, unlike the Er-analog where tie-line was found between Ba₂Er₃Cu₅O₆₊ₓ and Ba₄ErCu₅O₉.
a tie-line was instead found between Ba$_2$GdCu$_3$O$_6$+z and Ba$_6$GdCu$_3$O$_7$.

3.3. Implications for processing

For applications of phase equilibria to coated conductor processing, phase diagrams constructed under carbonate-free conditions should be employed. From examination of Figs. 1 and 2, there is a significant difference in the tie-line distributions occurring under carbonate-free conditions, relative to those occurring in the phase diagrams based on BaCO$_3$-derived starting materials [18–25]. Under carbonate-free conditions at a $p_{O_2}$ of 100 Pa, the Ba$_2$GdCu$_3$O$_6$+z–Ba$_6$GdCu$_3$O$_7$ tie line replaces a BaCuO$_{2z}$–Ba$_2$Gd$_2$Cu$_3$O$_5$ tie line in the BaO–Gd$_2$O$_3$–CuO$_2$ system; and the Ba$_2$ErCu$_3$O$_6$+z–BaErCu$_3$O$_5$ tie line replaces a BaCuO$_{2z}$–BaEr$_2$Cu$_2$O$_5$ tie line in the BaO–Er$_2$O$_3$–CuO$_2$ system. The net effect of this change is to expand the field of stability of Gd-213 and Er-213 toward the BaO-rich corner of the phase diagram. However, it is questionable as to whether this is an advantage for the R-213 processing. For example, as a result of the difference in the tie-line relationships, Ba$_4$ErCu$_3$O$_6$+z can coexist with Er-213. Because Ba$_4$RCu$_3$O$_6$ is atmospherically more sensitive than BaR$_2$CuO$_5$, its presence in R-213 and Er-213 toward the BaO-rich corner of the phase diagram. The net effect of this is to expand the field of stability of Gd-213 and Er-213 toward the BaO-rich corner of the phase diagram. However, it is questionable as to whether this is an advantage for the R-213 processing. For example, as a result of the difference in the tie-line relationships, Ba$_4$ErCu$_3$O$_6$+z can coexist with Er-213. Because Ba$_4$RCu$_3$O$_6$ is atmospherically more sensitive than BaR$_2$CuO$_5$, its presence in R-213 and Er-213 toward the BaO-rich corner of the phase diagram. The net effect of this is to expand the field of stability of Gd-213 and Er-213 toward the BaO-rich corner of the phase diagram.

4. Summary

We have investigated the phase relationships of the BaO–Er$_2$O$_3$–CuO$_2$ and the BaO–Gd$_2$O$_3$–CuO$_2$ systems at $p_{O_2}$ = 100 Pa (810°C). Sample preparation and handling was accomplished using a glove box filled with argon and an atmospherically-controlled furnace and apparatus. Similar to the Nd-, Sm- and Y-systems that we have reported previously [15–17], the presence of CO$_2$ affects the tie-line relationships. For example, the tie-line relationships among the four phases, BaEr$_2$CuO$_5$, Ba$_2$ErCu$_3$O$_7$, BaCuO$_{2z}$, and Ba$_4$ErCu$_3$O$_6$+z are different from the literature data. A comparison of the BaO–Gd$_2$O$_3$–CuO$_2$ and the BaO–Er$_2$O$_3$–CuO$_2$ systems indicates that due to the absence of the BaR$_2$O$_5$ phase, and the formation of R$_2$CuO$_5$ type phase instead of R$_2$Cu$_2$O$_5$ phases in the Gd-analog, the tie-line relations are different in the two systems.

Since phase diagrams of the BaO–R$_2$O$_3$–CuO$_2$ (R = lanthanides) systems are important for the coated-conductor development, systematic studies of diagrams of other analogs (i.e., R = Eu, Dy, Ho, Yb, Tm and Lu) under atmospheric-controlled conditions will continue.

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