Subsolidus phase relationships of the BaO–R$_2$O$_3$–CuO$_z$ (R = Tm and Yb) systems under carbonate-free conditions at $p_{O_2} = 100$ Pa, and $T = 750^\circ$C and 810$^\circ$C

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Abstract

For applications of phase equilibria to coated conductor processing, phase diagrams constructed under carbonate-free conditions should be employed. Using special apparatus and a procedure for preparing carbonate-free precursors based on BaO, phase diagrams of the BaO–Tm$_2$O$_3$–CuO$_z$ and BaO–Yb$_2$O$_3$–CuO$_z$ systems were determined at 100 Pa (0.1% $O_2$ by volume, 750$^\circ$C and 810$^\circ$C). The BaO–Yb$_2$O$_3$–CuO$_z$ system exhibits different features as compared to the Tm-analog. For example, the Yb-system does not contain the Ba$_4$RCu$_3$O$_{8.5+}$ phase. The absence of this phase affects the tie-line relations in the BaO-rich region of the phase diagram of the Yb-system. Furthermore, while the diagrams with relatively large R (i.e., R = Nd, Sm, Eu, Gd, Dy, Er) do not contain a tie-line between BaCuO$_2+$ and BaR$_2$CuO$_5$, this tie-line was found in the Yb-diagram, which has a much smaller R. In general, both the diagrams of the BaO–Tm$_2$O$_3$–CuO$_z$ and of the BaO–Yb$_2$O$_3$–CuO$_z$ systems prepared under carbonate-free conditions are different from those obtained using BaCO$_3$-derived starting materials.

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Keywords: High-$T_c$ superconductors; Solid-state reactions; Phase diagrams; X-ray diffraction

1. Introduction

Since the discovery of the high temperature superconductor oxides [1], considerable technological progress has been achieved in 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]. More recently, second-generation high-$T_c$ superconductor (HTS) tapes (also called HTS coated conductors) deposited on flexible coated-conductors have received much attention [7–11]. Second-generation superconductors are based on Ba$_2$YCuxO$_{6+z}$ and Ba$_2$RCuxO$_{6+z}$ materials (R = lanthanide-substituted variants) [12–15]. The Ba$_2$YCuxO$_{6+z}$ and Ba$_2$RCuxO$_{6+z}$ 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, HTS coated-conductor have great commercial potential for electric utility and high magnetic field applications. The efforts of the Superconductivity Partnership Initiative of the US Department of Energy have led to a substantial number of prototype applications [16].

Two HTS coated-conductor processes are furthest along in their technological development: the rolling-assisted biaxially textured substrate process (RABiTS) [7–9], and the ion beam-assisted deposition process (IBAD) [10,11]. Phase diagrams provide important data for both processes. Previously, we have reported phase diagram studies of the BaO–R$_2$O$_3$–CuO$_z$ systems (R = Nd [17], Sm [18], Y [19], Er, Gd [20], Dy, Ho and Eu [21]) under carbonate-free conditions at $p_{O_2} = 100$ Pa. The experimental conditions were selected to match RABiTS and IBAD processing conditions. Phase diagrams of the BaO–Tm$_2$O$_3$–CuO$_z$ [22,23] and BaO–Yb$_2$O$_3$–CuO$_z$ [24,25] systems are available in literature; however, partly because it is difficult to handle BaO, the majority of these diagrams were prepared using BaCO$_3$ as one of the starting reagents. The goal of the present paper is to report our studies of the R = Tm and R = Yb systems under conditions similar to our previous studies, i.e., $p_{O_2} = 100$ Pa, $T = 750^\circ$C and 810$^\circ$C, with BaO as a source

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2.1. Preparation of BaO

BaO starting material was produced from BaCO₃ (99.99% purity, metals basis) by vacuum calcination in a custom-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 μHg or less by a high capacity mechanical pump. The temperature of the sample was raised from room temperature to 1300 °C in 20 h, followed by an isothermal heat-treatment at 1300 °C for 10 h, and then cooled from 1300 °C to room temperature in 20 h. During vacuum calcination the pressure typically increased to ~10 mHg or less by a high capacity mechanical pump. The temperature of the sample was raised from room temperature to 1300 °C in 20 h, followed by an isothermal heat-treatment at 1300 °C for 10 h, and then cooled from 1300 °C to room temperature in 20 h.

2.2. Sample preparation

All sample weighings, homogenizations and pressings of pellets were performed inside the glove-box to avoid contamination with CO² and H₂O. 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.

The solid-state sintering method was used to prepare 28 samples each for the BaO–Tm₂O₃–CuO₃ system and for the BaO–Yb₂O₃–CuO₃ system (Table 1). Stoichiometric amounts of BaO, R₂O₃ (R = Tm and Yb) (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 annealings, 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 750 °C and 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.

2.3. X-ray powder diffraction

For X-ray phase analysis, specimens were loaded into a hermetic cell designed for air-sensitive materials [26]. The process of sample loading was performed inside an Ar-filled glove-box. X-ray 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. 1–4 give the phase diagrams of the BaO–Tm₂O₃–CuO₃ and the BaO–Yb₂O₃–CuO₃ systems. These diagrams appear to be relatively simple, but are different from those prepared using BaCO₃ [22–25], particularly in the Ba-rich region. Due to the substantially different ionic size of Tm³⁺ and Ba²⁺ (0.994 Å versus 1.42 Å) [28], respectively, 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–Tm₂O₃–CuO₃ system

3.1.1.1. The BaO–CuO₃ System. A review of the crystal chemistry and crystallography of the phases in the BaO–CuO₃ system was given by Wong-Ng and Cook [29], and therefore the details

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Table 1

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In the table, Ba stands for BaO, Tm/Yb stands for 1/2(Tm₂O₃) or 1/2(Yb₂O₃), and Cu stands for CuO. The numbers in the table correspond to mole fraction, %.

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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.
will not be discussed here. At both 750 °C and 810 °C, the compounds Ba₂CuO₃₊ₓ and BaCuO₂₊ₓ were found to be stable at pO₂ = 100 Pa [29–34]. The Ba₂CuO₃₊ₓ phase is atmospherically 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 [29]. 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. [34]. At 810 °C, we found that the reduced phase BaCu₂O₂₊ₓ was observed in addition to Ba₂CuO₃₊ₓ and BaCuO₂₊ₓ. Also, CuO was found to be reduced to Cu₂O. There is no evidence for the existence of the Ba₂Cu₃O₅₊ₓ or Ba₃Cu₅O₈₊ₓ phases [30]. The Ba₃CuO₄ phase, reported by Frase and Clarke [35] and Abbattista et al. [36,37] to be stable under very reduced conditions, was not detected in the present study. In contrast to the BaO–Nd₂O₃–CuO [17], BaO–Sm₂O₃–CuO [18], and the BaO–Eu₂O₃–CuO [21] systems where one observes the formation of the (Ba, R)₂CuO₃₊ₓ phase, no solid solution formation of the (Ba, Tm)₂CuO₃₊ₓ system was found due to the large difference in the ionic size of Ba and Tm [28].

3.1.1.2. BaO–Tm₂O₃. Different from the BaO–Y₂O₃ [19] and BaO–Er₂O₃ [20] systems, the Ba₃R₄O₉ but not BaR₂O₄ phase was found to be stable in the BaO–Tm₂O₃ system at both 750 °C and 810 °C. The Ba₂R₂O₅ and Ba₄R₂O₉-type phases as reported in the BaO–Y₂O₃–CuO [39] system (prepared with BaCO₃-derived starting materials [38]) are not stable here. The Y-analogs of these phases have been determined by Abbattista et al. [37] and DeLeeuw et al. [32] to correspond to Ba₂Y₂O₅·CO₂ and Ba₄Y₂O₉·2CO₂.

3.1.1.3. Tm₂O₃–CuO₂. At both 750 °C and 810 °C, only the Tm₂Cu₂O₅ phase was observed in the Tm₂O₃–CuO₂ diagram [39]. The R₂CuO₄ type phase only exists when R is relatively large (r₉³⁺ > r₆³⁺). As r₉³⁺ decreases beyond Gd (namely, from Dy to Lu), the R₂Cu₂O₅ type phase (orthorhombic, Pna₂₁) was found instead of R₂CuO₄ [13]. Furthermore, the reported reduced phase of the YCuO₂ structure type [40,41] was not found; presumably the oxygen partial pressure of pO₂ = 100 Pa is not sufficiently low to stabilize this phase.

3.1.1.4. BaO–Tm₂O₃–CuO₂. At both 750 °C and 810 °C, a total of four ternary oxides (Ba₂TmCu₃O₆₊ₓ, Ba₄TmCu₃O₈.₅₊ₓ, Ba₆TmCu₃O₁₀.₅₊ₓ, and the ‘green phase’ Ba₂Tm₂CuO₅) were found in the BaO–Tm₂O₃–CuO₂ system (Figs. 1 and 2). The formation of the compounds Ba₄RCu₃O₅₊ₓ and Ba₇RCu₃O₁₀.₅₊ₓ in the BaO-rich part of the diagram is similar to that in the...
BaO–Yb2O3–CuO2 system. For applications of phase equilibria to coated conductor processing, phase diagrams constructed under carbonate-free conditions should be employed. An examination of Figs. 1–4 phases [19], Ba4YbCu3O10.5+ was reported to be orthorhombic (Immm, a = 3.9830(2) Å, b = 4.0986(2) Å, and c = 21.571(1) Å) when prepared in air [44]. While the Ba4YbCu3O8.5+ phase can be prepared at pO2 = 0.1 MPa or pO2 = 0.022 MPa (air) [44,52], it cannot be prepared at pO2 = 100 Pa. The ‘green phase’ BaYb2CuO3 is isostuctural to BaTm2CuO5 [13].

3.2. Phase Compatibilities

3.2.1. BaO–Tm2O3–CuOz

The tie-lines determined near the CuO2 and Tm2O3 regions are in agreement with those determined in most other BaO–R2O3–CuOz diagrams, whether prepared using BaCO3, BaO2, BaO, or Ba(NO3)2. However, the BaO-rich regions of the diagrams are substantially different from each other. This diagram of the Tm-system prepared using BaO is somewhat different to that of the BaO–Y2O3–CuO system reported by us [19]. The tie-line relationships around the 213 phase which involve the four phases, Ba3TmCu3O8.5+, Ba2TmCuO5, BaCuO2+, and Ba2TmCuO4, are also different from the literature data. For example, in the present study, the Ba2TmCu3O6.5+ phase is found to be compatible to the Ba4TmCu3O10 phase, whereas most literature phase diagrams of the BaO–R2O3–CuO systems involve a tie-line between BaCuO2+ and Ba2CuO3+ [13,19,22,23,53–58]. The Ba2RCu3O6.5+–Ba3RCu3O8 tie-line was also found in our previous studies of the Nd-, Sm-, Eu, Dy-, Ho-, Y-, and Er-systems [17–21], and during the investigation of the melting equilibria of the BaO–Y2O3–CuO system [59]. 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–Yb2O3–CuOz

The tie-line distribution in the Ba-poor region of the BaO–Yb2O3–CuO system, as shown in Figs. 3 and 4, is in general similar to that found in the BaO–Tm2O3–CuO system. Unexpectedly, we found that at both 750 °C and 810 °C, there is a tie-line connecting the BaCuO2+ phase to the ‘green phase’, BaYb2CuO5. This is different from other BaO–R2O3–CuO systems while the size of R3+ is larger than that of Yb3+. Therefore, whether a tie-line exists between Ba2CuO3+ and BaCuO2+, or between Ba2RCu3O6.5+, and a barium-rich phase appears to depend on the condition of preparation and the size of R3+. A comparison of the BaO–Yb2O3–CuO diagrams (Figs. 1 and 2) to the BaO–Tm2O3–CuO diagrams (Figs. 3 and 4) indicates that the absence of the Ba4YbCu3O8.5+ phase affects the tie-line relations in the region bounded by BaCuO2, Ba2YbCu3O6.5+, BaYbCu2O5, and Ba6YbCu3O10.5+. All ternary oxides are compatible with at least four other phases. In the case of BaYb2CuO5, seven tie-lines were found to originate from it. In the BaO-rich region, tie-lines are found between BaO and Ba6YbCu3O7.
shows a significant difference in the tie-line distributions occurring under carbonate-free conditions, relative to those occurring in the phase diagrams based on BaCO3-derived starting materials [22–25]. Under carbonate-free conditions at a \( p_{\text{CO}_2} = 100 \text{ Pa} \), the Ba2TmCu3O6+–Ba4TmCu3O9+ tie-line replaces a BaCuO2+–Ba2TmCu3O5+ tie-line in the BaO–Tm2O3–CuO system; and a BaCuO2+–Ba2Yb2Cu3O9+ tie-line replaces the Ba3YbCu3O7 (R = lanthanides) system. The net effect of this difference is that in the Tm-case, there is an expansion of the field of stability of Tm-213 towards the BaO-rich corner of the phase diagram as compared to the Yb-213 phase; Ba4TmCu3O8.5+ is atmospheric more sensitive than Ba4RCu3O8.5+, its presence can coexist with Tm-213. However, because Ba4R2CuO8.5+ is present during the RABiTS and IBAD processes to avoid bulk compositions in this region.

4. Summary

We have investigated the phase relationships of the BaO–Tm2O3–CuO and the BaO–Yb2O3–CuO systems at \( p_{\text{CO}_2} = 100 \text{ Pa} \) under both 750°C and 810°C. Sample preparation and handling were accomplished using a glove-box filled with argon and an atmospherically-controlled furnace and apparatus. Similar to the Nd-, Sm-, Eu-, Gd-, Dy-, Ho-, Y-, and Er-systems that we have reported previously [17–21], the presence of CO2 affects the tie-line relationships. For example, the tie-line relationships among the four phases, BaTm2CuO5, Ba2TmCu3O5+, BaCuO2+, and Ba4TmCu3O8.5+ are different from the literature data. A tie-line between Ba2TmCu3O5+ and Ba4TmCu3O8.5+ was observed. In the Yb-system, a tie-line between BaYb2CuO9+ was found instead. It appears that whether a tie-line exists between BaR2CuO5 and BaCuO2+, or between Ba2RCu3O6+ and a barium-rich phase appears to depend on the condition of preparation and the size of \( R^{3+} \). In addition, due to the absence of the BaYbCu3O8.5+ phase in the Yb-analog, the tie-line relations are different in the BaO–Yb2O3–CuO and the BaO–Tm2O3–CuO systems.

Phase diagrams of the BaO–R2O3–CuO (R = lanthanides) systems are important for coated-conductor development, and it is anticipated that systematic studies of diagrams of these systems under relevant atmospherically-controlled conditions will continue.

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References