LETTER TO THE EDITOR

The Stabilization of β-Bi$_2$O$_3$ by CeO$_2$

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The subsolidus phase relations of the binary system Bi$_2$O$_3$–CeO$_2$ have been investigated. It was found that CeO$_2$ forms neither a compound nor a solid solution with Bi$_2$O$_3$. CeO$_2$, however, can stabilize β-Bi$_2$O$_3$ over a wide composition range. The stabilization depends on the contents of CeO$_2$ as a second phase and on the heat treatment. A stabilization mechanism is proposed. © 1996 Academic Press, Inc.

The tetragonal modification of bismuth oxide, β-Bi$_2$O$_3$, forms at about 920 K (1–3) on cooling the cubic high-temperature phase δ-Bi$_2$O$_3$. It is metastable at low temperatures with respect to the monoclinic α-Bi$_2$O$_3$ and transforms to this phase at about 870 K (1). It should be mentioned that at low temperatures metastable β-Bi$_2$O$_3$ can be obtained by the thermal decomposition of Bi$_2$O$_3$CO$_2$ (1). Moreover, a number of nonstoichiometric phases (known as β^*) can be stabilized by various oxides as in the systems Bi$_2$O$_3$–TeO$_2$ (4, 5), Bi$_2$O$_3$–Sb$_2$O$_3$ (6), Bi$_2$O$_3$–TiO$_2$ (7), Bi$_2$O$_3$–Y$_2$O$_3$ (7), Bi$_2$O$_3$–HfO$_2$ (8), Bi$_2$O$_3$–Ln_2O$_3$–TeO$_2$ (Ln = La, Sm, Gd, Er) (9), Bi$_2$O$_3$–PbO–PbF$_2$ (10), and Bi$_2$O$_3$–PbF$_2$ (11). In all these cases, the stabilization is due to the incorporation of the added cations into the Bi$_2$O$_3$ structure, forming solid solutions. In the present paper it is shown that β-Bi$_2$O$_3$ can be stabilized by CeO$_2$ over a wide composition range in the system Bi$_2$O$_3$–CeO$_2$. The stabilization mechanism is probably different from other cases in not forming solid solutions.

In the system of $\frac{1}{2}$ Bi$_2$O$_3$–CeO$_2$ a series of samples with molar fractions x = 0.05, 0.08, 0.09, 0.10, 0.12, 0.15, 0.20, 0.50, 0.75, and 0.80 CeO$_2$ were prepared by solid state reaction of appropriate amounts of Bi$_2$O$_3$ (Heraeus, 99.999%) and CeO$_2$ (Heraeus, 99.9%). The powders were carefully mixed, put in a corundum or a platinum crucible, fired at 820°C for 3 to 5 days in air, and finally quenched to room temperature. The X-ray powder diffraction (XRPD) patterns showed that all these samples consist of multi-

phase mixtures, one of the phases always being CeO$_2$. The crucible materials have no influence on reactions. Figure 1 shows the XRPD patterns for samples with x = 0.08, 0.12, and 0.15. The phase relations of the system Bi$_2$O$_3$–CeO$_2$ obtained by quenching are shown in Fig. 2a. Three different regions can be distinguished. Region I ($0 \leq x \leq 0.08$) contains α-Bi$_2$O$_3$ and CeO$_2$; region II ($0.8 < x \leq 0.15$) exhibits three phases, α-Bi$_2$O$_3$, β-Bi$_2$O$_3$, and CeO$_2$. Finally, in region III ($x > 0.15$) β-Bi$_2$O$_3$ and CeO$_2$ are observed.

It should be noted that the phase relations in Fig. 2a do not represent an equilibrium state, since no three-phase field can exist in a binary system. The boundaries of the regions (Fig. 2a) are temperature dependent. The relations obtained by long time annealing at 400°C are shown in Fig. 2b. The β-Bi$_2$O$_3$ phase in region II transforms to α-Bi$_2$O$_3$ so that α-Bi$_2$O$_3$ + CeO$_2$ are found within $0 \leq x \leq 0.15$. Region III $x > 0.15$ remains unchanged with β-Bi$_2$O$_3$ + CeO$_2$.

To determine the lattice parameters, the XRPD data were collected by step scanning with steps of 0.02° 2θ and counting times >10 s per step. NBS RSM640 Si was added as internal standard. It was found that the lattice parameters of β-Bi$_2$O$_3$ are independent of the CeO$_2$ concentration with a = 7.741 ± 0.002 Å and c = 5.634 ± 0.001 Å. These values are in good agreement with those previously reported for pure β-Bi$_2$O$_3$ (12, 13). For α-Bi$_2$O$_3$ and CeO$_2$, the lattice parameters are also independent of the compositions within similar estimated standard deviations (±0.002 Å, or 2θ = ±0.01°) and are in good agreement with the known values (14).

The persistence of CeO$_2$ in all samples and the constant lattice parameters of α-Bi$_2$O$_3$, β-Bi$_2$O$_3$, and CeO$_2$ indicate that there exists no measurable solid solutions in the binary system Bi$_2$O$_3$–CeO$_2$ under the conditions of the present investigation. This is also evident from the fact that in the sample with 5% CeO$_2$ the phase CeO$_2$ was clearly observed. Additional evidence is that there is no change of reflection intensities of CeO$_2$ after β converts into α by long time

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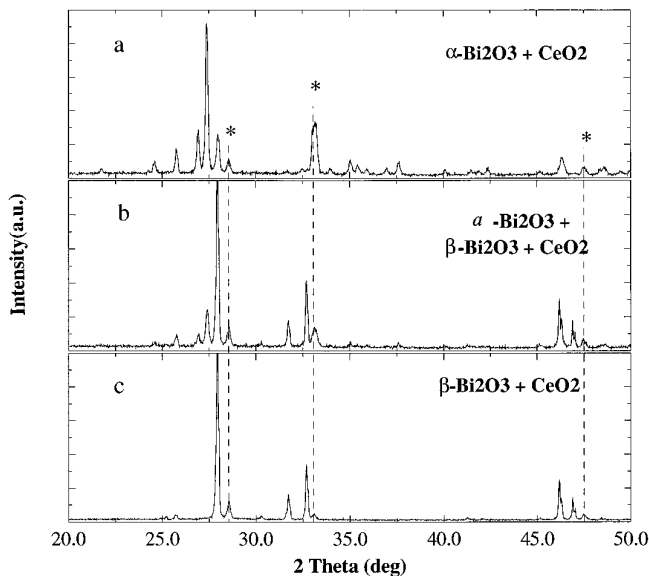**FIG. 1.** XRPD patterns for compositions $(BiO_{1.5})_{1-x}(CeO_2)_x$, (a) $x = 0.08$; (b) $x = 0.12$, (c) $x = 0.15$. The peaks marked by "+" are due to CeO_2. Note the CeO_2 reflection (200) and α-Bi_2O_3 reflections (-122) and (121) overlap at about $2\theta = 33.05°$.

annealing even in the sample for $x = 0.15$, where β dominates before annealing.

To explain the stabilization of β-Bi_2O_3 by CeO_2, two rather different explanations may be considered. First, β-Bi_2O_3 could be stabilized by the incorporation of CeO_2 into Bi_2O_3 in amounts too small to be detected by the methods applied. Second, Bi_2O_3 is stabilized just by the presence of the phase CeO_2. The latter explanation appears more probable to the authors and, therefore, is presented subsequently in more detail.

It is based on the crystal structural relationship of β-Bi_2O_3 and CeO_2. β-Bi_2O_3 exhibits an ordered fluorite-type structure with lattice parameters $a = 7.741$ Å and $c = 5.563$ Å. The ordering along [110] of β-Bi_2O_3 suggests $a_c \approx \sqrt{2}/2a_t \approx 5.47$ Å, which is close to $a \approx 5.41$ Å of the

fluorite type CeO_2. Hence, CeO_2 may act as an extrinsic nucleus for the formation of β-Bi_2O_3. The growth of β-Bi_2O_3 on the surface of CeO_2 grains probably lowers its free energy of formation compared to that of "normal" α-Bi_2O_3 below 870 K. On cooling, δ-Bi_2O_3 first transforms into β-Bi_2O_3, and some of the β grains grow on the surface of CeO_2 particles. On further cooling, these grains will keep the β structure, while those without a CeO_2 core will transform into α-Bi_2O_3 below 870 K. The transformation from β to α depends obviously on both the amount of CeO_2 and the cooling procedure. If this model applies, CeO_2 would be a good substrate to grow thin films of β-Bi_2O_3.

It is interesting to compare Ce^{4+} with other cations with respect to their influence on Bi_2O_3. The small tetravalent ions $M^{4+} = Si^{4+}$, Ti^{4+}, and Ge^{4+} form as stable phases no solid solutions but only stoichiometric compounds $Bi_{12}MO_{20}$ with the Sillenite structure, which contains these ions as ordered MO_4 tetrahedra (15–18). Other ions with different valencies and sizes such as Zn^{2+}, Pb^{2+}, B^{3+}, Al^{3+}, Zr^{4+}, and P^{5+} from solid solution ranges with γ-Bi_2O_3 structure (19). Hence, Ce^{4+} seems exceptional in forming neither an ordered Sillenite phase nor a γ-Bi_2O_3-type solid solution. Instead, it stabilizes β over a wide composition range.

Finally, we did not find the fluorite-type solid solution as reported by Hund (20) in the system Bi_2O_3–CeO_2 with 0 to 40 mol% Bi_2O_3.

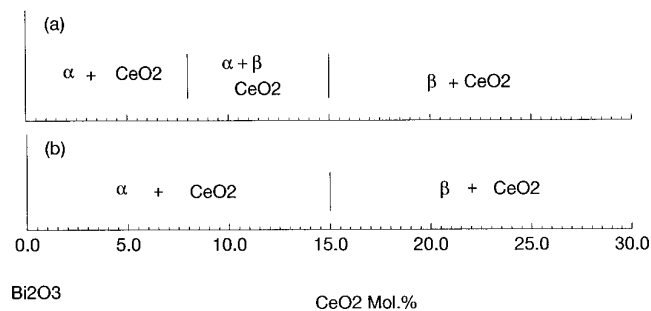**FIG. 2.** Phase relations in the system $BiO_{1.5}$–CeO_2 (a) quenched from 820°C and (b) annealed at 400°C for 1 week.

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