Structural and Dynamical Studies of δ-Bi$_2$O$_3$ Oxide Ion Conductors

III. Phase Relationships in the System (Bi$_2$O$_3$)$_{1-x}$(*M*$_2$O$_3$)$_x$ as a Function of Pressure and Temperature (*M* = Y, Er, or Yb)

P. D. BATTLE,*,[1] G. HU,*,[2] L. M. MORONEY,† AND D. C. MUNRO*

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom, and †NSLS, Brookhaven National Laboratory, Upton, New York 11973

We report the results of a structural investigation of the nonstoichiometric solid solutions (Bi$_2$O$_3$)$_{1-x}$(*M*$_2$O$_3$)$_x$ (*M* = Y, Er, or Yb) treated at temperatures of between 298 and 1023 K and at pressures of up to 4 GPa. For *x* = 0.25 and *M* = Er or Y, 4 GPa pressure at 873 K causes the fluorite-related phase stable under ambient conditions to transform to a monoclinic phase which on subsequent annealing transforms to a rhombohedral phase isostructural with that adopted by the solid solution (Bi$_2$O$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$ under ambient conditions. For *x* = 0.4 and *M* = Er or Y, application of 4 GPa at 1073 K causes the fluorite phase to undergo a distortion to another rhombohedral structure with a smaller unit cell. No transitions were found in the Yb^{3+}-doped system. © 1987 Academic Press, Inc.

Introduction

The high-temperature δ-phase of Bi$_2$O$_3$ (stable above 1003 K) is the best oxide ion conductor known (*1*), with a conductivity of ~1 Ω^{-1} cm^{-1} at 1023 K, several orders of magnitude greater than that of calcium-stabilized zirconia, the benchmark for oxide ion conductors. The high conductivity is lost when the fluorite-related δ-phase transforms to α-Bi$_2$O$_3$ below 1003 K. However, the fluorite phase can be retained at room temperature if Bi$_2$O$_3$ is doped with the sesquioxides of the smaller rare earths or yttrium to form the nonstoichiometric solid solutions (Bi$_2$O$_3$)$_{1-x}$(*M*$_2$O$_3$)$_x$ with 0.25 < *x* < 0.4. The exact range of dopant concentra-

tion that stabilizes the fluorite phase depends on *M*, but it is generally true that the smaller the radius of the dopant cation, the lower the concentration needed to stabilize the fluorite phase (*2*). The conductivity of the solid solutions is never as high as that of undoped δ-Bi$_2$O$_3$, but they do retain a reasonable ionic conductivity down to low temperatures (~10^{-2} Ω^{-1} cm^{-1} at 773 K). When Bi$_2$O$_3$ is doped with the oxide of a larger cation, for example, isovalent Sm$_2$O$_3$ or aliovalent SrO, the resultant solid solution has a rhombohedral crystal structure (*2, 3*) which also permits fast anion transport. This structure consists of blocks of metal oxide separated by planes within which the mobile anions are assumed to lie. X-ray diffraction experiments (*5*) have established that there is a partial ordering of the Bi^{3+} and Sr^{2+} ions in the blocks of the strontium-doped system, but only a fraction of the anions have been located.

[1] Author to whom correspondence should be addressed.

[2] On leave from the Research Institute of Synthetic Crystals, P.O. Box 733, Beijing, The People's Republic of China.

It has been shown that rhombohedral (Bi$_2$O$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$, stable for $0.2 < x < 0.35$ at room temperature, transforms to a fluoritelike phase at high temperature (2). (Bi$_2$O$_3$)$_{0.6}$(Sm$_2$O$_3$)$_{0.4}$ adopts the fluorite structure at all temperatures investigated to date. It thus appears that increasing the dopant concentration of a relatively large dopant cation stabilizes the defect-fluorite phase with respect to the rhombohedral phase at room temperature.

Neutron scattering experiments (4, 5) on the nominally fluorite (Bi$_2$O$_3$)$_{1-x}$(M$_2$O$_3$)$_x$ (M = Y, Er, and Yb) solid solutions have revealed substantial short-range ordering, the extent of which increases with x. This result was interpreted in terms of a model involving the formation of microdomains of the rhombohedral phase within the fluorite structure. This apparent increase in microdomain formation with increasing x is in conflict with the behavior observed in (Bi$_2$O$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$, where the rhombohedral phase becomes less stable as x increases. This anomaly can be resolved if we assume that different factors stabilize the rhombohedral phase in the two cases. It is always dangerous to rely too heavily on ionic-size arguments when discussing the structural chemistry of bismuth compounds, because the "lone pair" of electrons on the Bi^{3+} ion can play a very varied rôle and hence the ionic radius of Bi^{3+} is badly defined. However, it is reasonable to
* postulate that there is a value for the average cation radius in (Bi$_2$O$_3$)$_{1-x}$(M$_2$O$_3$)$_x$ above which the fluoritelike structure is unstable with respect to the rhombohedral phase. This value is never reached when M = Y, Er, or Yb; it is reached for $0.35 < x < 0.4$ when M = Sm. This is consistent with the unit cell parameter of (Bi$_2$O$_3$)$_{0.6}$(Sm$_2$O$_3$)$_{0.4}$, that is, ~5.517 Å (2), being larger than that of any of the Er^{3+}-doped fluorite solid solutions. It is not clear whether the instability of the fluorite phase of the M = Y, Yb, and Er solid solutions at

low dopant concentrations is induced by size effects or electronic effects; whatever the cause of the instability, it does not lead to the adoption of the rhombohedral phase (6, 7) and this leads us to believe that the effect may be a cooperative transition driven by the stereochemical activity of the lone pairs of electrons on the Bi^{3+} ions, rather than a size effect.

The formation of rhombohedral microdomains at high dopant concentrations when M = Y, Er, or Yb clearly cannot be explained by the same cation-size argument that we used above; the average cation size decreases as microdomain formation increases in these systems. The cause of the defect ordering, or microdomain formation, may well be electronic in origin; it is reasonable to expect the spherical Y^{3+} and Er^{3+} ions to lie in regular coordination sites, unlike Bi^{3+} with its lone pair of electrons. We have discussed this previously (4). A close structural relationship between the anion sublattice in the rhombohedral phase and that in the defect-fluorite phase would be consistent with the transition between the two phases seen in the system (Bi$_2$O$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$. In order to account for the behavior of (Bi$_2$O$_3$)$_{1-x}$(Yb$_2$O$_3$)$_x$, where the extent of microdomain formation is relatively small, we assume that there is a critical size for the dopant cation and that cations smaller than this size cannot stabilize even small microdomains of the rhombohedral phase; Yb^{3+} must approach this limiting size.

A model of structural behavior like that given above clearly needs to be tested experimentally, and one obvious way of doing this, when the model depends partly on arguments based on unit cell parameters and ionic size, is to apply pressure to the system. In particular, the adoption of the fluorite structure is favored at high temperature, as evidenced by the behavior of Bi$_2$O$_3$ itself and by that of the solid solutions (Bi$_2$O$_3$)$_{1-x}$(Sm$_2$O$_3$)$_x$ (2). If this phenomenon

is a volume effect, that is, the fluorite phase is stabilized by the thermal expansion of the structure, then it is reasonable to expect the fluorite phases $(Bi_2O_3)_{1-x}(M_2O_3)_x$, where M = Y, Er, or Yb, to transform to the rhombohedral phase under pressure. The remainder of this paper describes the results of experiments we performed to test this hypothesis.

Experimental

The samples of fluorite-phase solid solutions subjected to high pressures in this work were the same samples that had been used in earlier neutron scattering experiments, and their preparation has been described previously (4, 5, 8). About 45 mm³ of each sample, packed in thin-walled platinum tubes of diameter 3.76 mm with platinum end plugs, was subjected to conditions of elevated pressure (4 GPa) and temperature (873 or 1073 K) in a conical double-piston apparatus (9). After heating for 1 hr, the samples were cooled to room temperature under pressure. The X-ray powder diffraction pattern of the product was recorded, and the product was then annealed at ambient pressure at 373 K for 1 hr before another X-ray pattern was recorded at room temperature. This annealing procedure was then repeated at 100 K intervals in the temperature range $373 < T < 1073$ K.

Results

Our neutron scattering studies on Y^{3+}-and Er^{3+}-doped Bi_2O_3 indicated (5) that the two systems are structurally very similar, and to some extent the results of our high-pressure experiments reinforce this conclusion. Twenty-seven percent Y-doped Bi_2O_3 sample transformed to a new phase, M, after treatment at 4 GPa pressure and 873 K. On annealing, M transformed to a rhombohedral phase, R_1, at 573 K and R_1 reverted to a face-centered cubic fluoritelike phase, F, at

973 K (Fig. 1). The X-ray diffraction pattern of R_1 could be indexed in the space group $R\bar{3}m$ with unit cell parameters a = 3.94(1), c = 27.24(9) Å (hexagonal setting). Thus R_1 appears to be isostructural with the rhombohedral phase found at room temperature in the phase diagram of $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$ for $0.2 < x < 0.35$. The structure of phase M is less clear, but we believe that it is a monoclinic distortion of R_1. The strongest lines in the pattern are listed in Table I. There are not enough well-resolved peaks in the X-ray pattern to permit refinement of the monoclinic unit cell, which we believe to have $a \sim b \sim 4$ Å, $c \sim$ 27.2 Å, and $\beta \sim 120°$. The unit cell can usefully be thought of as a distortion of an R_1-type unit cell, the symmetry of which has first been lowered from rhombohedral to trigonal. Twenty-five percent Er-doped Bi_2O_3 sample also transformed to phase M after treatment at 4 GPa and 873 K (Fig. 2).
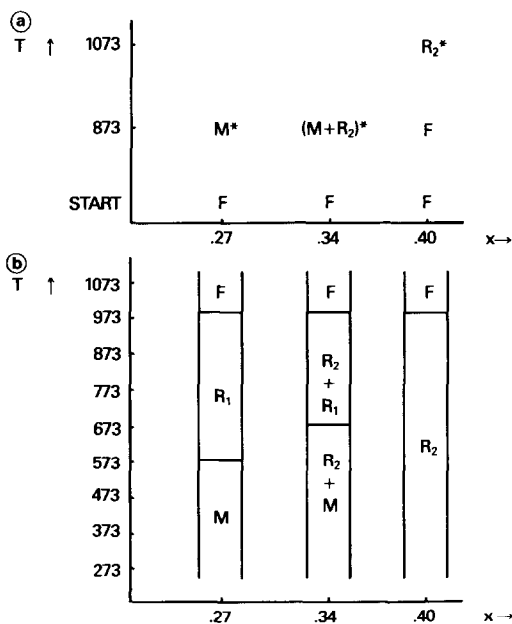

FIG. 1. A summary of the phases found in $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ as a function of temperature and pressure. (a) Treatment at 4 GPa and (b) after annealing marked products (*) at atmospheric pressure.

TABLE I

OBSERVED X-RAY
DIFFRACTION
PATTERN
OF PHASE M OF
$(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$

d (Å)	I
4.32	12
3.43	13
3.34	10
3.27	21
3.20	43
3.06	76
2.97	100
2.89	76
2.81	70
2.31	11
2.24	27
2.18	22

In this case M transformed to a very poorly crystalline R_1 phase at 673 K and an increasing amount of cubic fluorite F was seen to coexist with R_1 after annealing at 773 and 873 K. Only the fluorite phase was present after annealing at 973 K. Treatment of both 27% Y- and 25% Er-doped Bi_2O_3 at 4 GPa and 1073 K left the initial fluorite phase unchanged. However, 40% Y- and 40% Er-doped Bi_2O_3 were both unchanged after treatment at 4 GPa and 873 K, but they both transformed to a phase R_2 after treatment at 4 GPa and 1073 K. All the lines in the X-ray pattern from the Er-doped material could be indexed on a rhombohedral unit cell with $a = 3.856(1)$ Å, $\alpha = 58.6(2)°$ or $a = 3.773$, $c = 9.545$ Å in the hexagonal setting. The former representation shows that the R_2 phase is simply a rhombohedrally distorted fluorite whereas the latter provides a connection with the structure of R_1, that is, the unit cell of R_1 is a supercell of R_2 with $c_{R_1} \sim 3c_{R_2}$ and $a_{R_1} \sim a_{R_2}$. In the case of the 40% Y-doped sample, the X-ray pattern showed a small number of weak peaks which could not be indexed on the rhombohedral R_2 cell. It is not clear

whether these reflections stem from a small distortion to lower symmetry or from the presence of a second phase. The unit cell parameters derived for the R_2 phase in this sample are $a = 3.787$, $c = 9.601$ Å (hexagonal setting). Phase R_2 reverted to a cubic symmetry for both Y- and Er-doped samples on annealing at 973 K. A sample of 34% Y-doped Bi_2O_3 transformed largely to the R_2 structure after treatment at 4 GPa and 873 K although traces of phase M were also present. The latter transformed to phase R_1 at 673 K and the entire sample reverted to the fluorite structure on annealing at 973 K. The unit cell parameters for phase R_1 in this sample were $a = 3.956(7)$, $c = 27.53(9)$ Å and those for R_2 were $a = 3.806$, $c = 9.626$ Å. We were unable to induce any phase transitions by the application of pressure to fluorite solid solutions of bismuth oxide and ytterbium oxide.
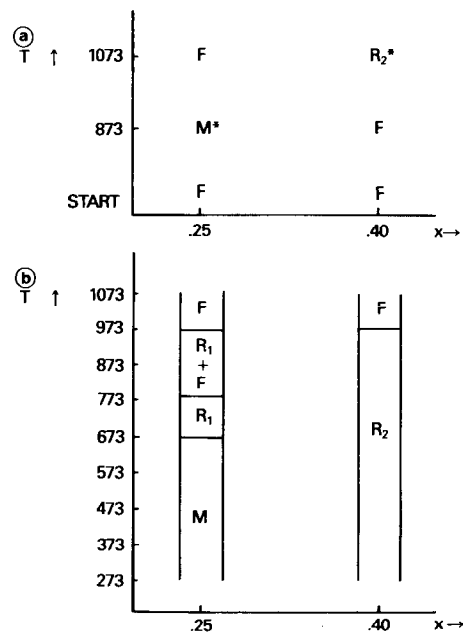

FIG. 2. A summary of the phases found in $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ as a function of temperature and pressure. (a) Treatment at 4 GPa and (b) after annealing marked products at atmospheric pressure.

Discussion

The results of our experiments support many of the ideas we put forward in the Introduction of this paper. In particular, the application of high pressure does convert cubic Bi_2O_3 doped with 25% Er or 27% Y to the rhombohedral structure, now labelled R_1, that is adopted by $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$ over a wide composition range. The volume per formula unit in the fluorite phases of these two materials is 82.24 (Er) and 82.21 $Å^3$ (Y) (4, 5), whereas the corresponding figures for the R_1 phases are 81.08 and 81.35 $Å^3$, respectively. As expected, the application of pressure produces a decrease in volume and under these conditions the fluorite phase transforms to the rhombohedral phase as we predicted. Indeed, the application of pressure initially drives the system to the previously unobserved, low-symmetry phase M. This phase then transforms to the R_1 structure on annealing, and on further annealing this exhibits the anticipated cubic/R_1 phase transition. The same transition could have been brought about by increasing the size of the dopant cation, and we can perhaps consider the application of pressure as a means of changing the relative ionic radii of Bi^{3+} and Y^{3+}. The two ions have different polarizabilities because of their differing electronic structures and they therefore accommodate the applied pressure in different ways, thus changing their effective radii. All our data, and those of Iwahara et al. (2), suggest that the fluorite phase is stabilized in these systems by low pressures and high temperatures, i.e., it is the high-volume phase. This is consistent with our previous observation (4) that the extent of microdomain formation in $(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$ decreases between room temperature and 1023 K.

The transformation of the 40%-doped samples to phase R_2 rather than R_1, and the intermediate behavior of the 34%-doped sample, is interesting, particularly when considered with the null results noted above for the Yb-doped samples. These results suggest that there is a critical cation size in these solid solutions and that the R_1 phase will not form if the average cation size is below the critical value. It may be that the structures of R_1 and R_2 are similar in the xy plane, but that R_1 exhibits a superlattice ordering in the z direction. As we suggest above, the inability of small cations to stabilize phase R_1 might be the reason why only limited microdomain formation occurs in the Yb-doped system.

Our discussion so far of the effects of pressure on these solid solutions has centered on the cation sublattice, whereas our interest in them really stems from the high ionic conductivity of the anion sublattice. The contribution of this work to an understanding of the microdomain formation on the latter sublattice is simply to demonstrate that transitions from the cubic fluorite phase to phase R_1 can be made to occur in the Y- and Er-doped systems, and that R_1 represents a more compact packing, as might be required by a high concentration of relatively small, unpolarizable, spherical Y^{3+} and Er^{3+} ions. Phase R_2 also represents a more efficient use of space than the fluorite structure of course, the formula unit volumes being 78.45 and 79.83 $Å^3$ respectively for $(Bi_2O_3)_{0.6}(Er_2O_3)_{0.4}$. The reason that the temperature needed to produce a phase transformation increases with Er and Y dopant concentration is not clear, but it may be because the transition to a rhombohedral phase is hindered by the presence within each crystallite of relatively large but randomly oriented rhombohedral microdomains which have a low oxide-ion mobility associated with them.

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