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Structural and Dynamical Studies of δ-Bi_2O_3 Oxide Ion Conductors. V. A Study of the System $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ by ^{151}Eu Mössbauer Spectroscopy

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Cubic ($x = 0.3$) and rhombohedral ($x = 0.2$) phases have been prepared in the solid solution $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$. The cubic material transformed to the rhombohedral form when subjected to a pressure of 4 GPa at a temperature of 873 K; at 4 GPa and 1073 K the transformation was to a phase of apparently monoclinic symmetry. ^{151}Eu Mössbauer spectroscopy has been used to study all three forms of $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ in order to estimate the extent of anion-vacancy ordering in the solid solution. The Mössbauer linewidth from all samples is lower than that measured for C–Eu_2O_3, suggesting that the Eu atoms in these compounds have a single, well-defined, local environment.

Introduction

The high-temperature δ phase of Bi_2O_3 (stable above 1003 K) is the best oxide ion conductor known (*1*) with a conductivity of $\sim 1\ \Omega^{-1}\ cm^{-1}$ at 1023 K, several orders of magnitude greater than that of calcium-stabilized zirconia. The high conductivity is lost when the fluorite-related δ phase transforms to α-Bi_2O_3 below 1003 K. However, the anion-deficient fluorite phase can be retained at room temperature if Bi_2O_3 is doped with the sesquioxides of the smaller rare earths or yttrium to form the solid solutions $(Bi_2O_3)_{1-x}(M_2O_3)_x$; the exact range of dopant concentration (x) that stabilizes the cubic fluorite phase depends on the nature of 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 δ-Bi_2O_3, but they do retain a reasonable ionic conductivity down to lower temperatures ($\sim 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 773 K). When the dopant concentration is lowered or when the dopant cation is relatively large, the resulting solid solution has a rhombohedral crystal structure (*2, 3*) which also permits fast anion transport. We have previously shown (*4*) that the fluorite phase can be converted to the rhombohedral phase for M = Y and Er (but not Yb) by the application of high pressure.

Structural studies of the fluorite-related phases have been carried out using neutron diffraction techniques (*5–8*). These experiments lead to a description of the average unit cell of the material. More recent experiments (*9–11*) have attempted to elucidate the immediate environments of the Bi^{3+} and M^{3+} cations because this local structure is likely to play a major role in determining the transport properties of the solid solu-

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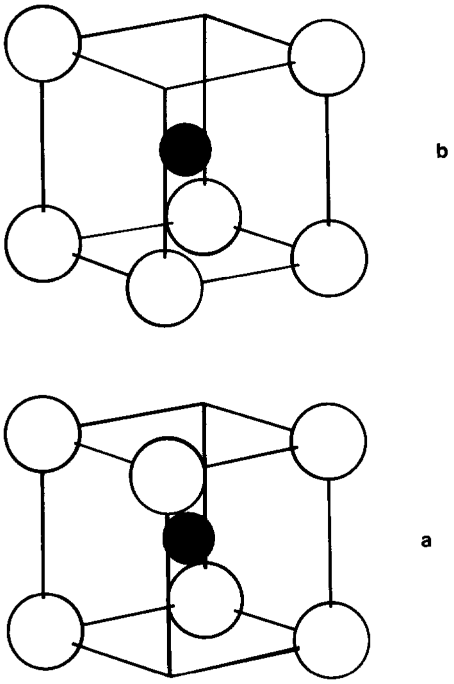

FIG. 1. The idealized geometries of the cation sites in the C-type rare-earth oxide structure. The cation lies at the center of a cube surrounded by six anions and (a) a ⟨111⟩ vacancy pair or (b) a ⟨110⟩ vacancy pair.

tion. EXAFS measurements (*10*) showed that the local environment of M^{3+} is considerably more regular than that around Bi^{3+}, and ^{89}Y magic angle spinning NMR spectroscopy has been used to compare the environment of Y^{3+} ions in the solid solution with those found in the C-type oxide Y_2O_3. In the C-type oxide structure, which can also be regarded as an anion-deficient fluorite structure, the trivalent cations occupy two distinct sites, the idealized geometries of which are shown in Figs. 1a and 1b. The site illustrated in Fig. 1a is surrounded by oxide ions at six of the eight corners of a cube, the two vacant corners lying at opposite ends of a body diagonal of the cube; the site drawn in Fig. 1b also has six-coordination, but now the vacant corners of the cube lie along a face diagonal. NMR spectroscopy showed that the Y^{3+} ions in the fluorite-related phase $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ preferentially occupy the site with the vacancy pair along ⟨111⟩ rather than ⟨110⟩. This result was consistent with a previous suggestion (*6*) that the lone pair of Bi^{3+} might be better accommodated if the host cation occupied (110)-type sites in the solid solution.

Mössbauer spectroscopy is another technique that allows us to study the local environment of a cation. Previous attempts to prepare the cubic solid solution $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ (*12, 13*) were unsuccessful, possibly because a low level of dopant ($x = 0.25$) was used despite the relatively large size of the Eu^{3+} ion. We have completed a study of this system over a range of x values and we have successfully prepared both the rhombohedral and cubic forms and studied their interconversion under pressure. Furthermore, we have studied our materials by ^{151}Eu Mössbauer spectroscopy in order to compare the environment of the rare-earth ion in the solid solution with that found in C–Eu_2O_3.

Experimental

Polycrystalline samples of $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ were prepared for $x = 0.2$ and 0.3 by firing the appropriate stoichiometric quantities of Bi_2O_3 and dried Eu_2O_3 (Johnson Matthey Chemicals, "Specpure" reagents) in a platinum crucible at 1073 K for 10 hr, 1273 K for a further 24 hr, and, finally, 773 K for 24 hr. High-pressure experiments were conducted on the product $x = 0.3$ in a conical double-piston apparatus (*14*). Approximately 50 mm^3 of sample was packed in a thin-walled platinum tube fitted with platinum end plugs and subjected to a pressure of 4 GPa at either 873 or 1073 K for 1 hr before being allowed to cool to room temperature under pressure. All products were characterized by X-ray powder diffraction. ^{151}Eu Mössbauer spectra were obtained for selected products at temperatures between 78 and 773 K using established techniques. The source matrix was $^{151}SmF_3$. The high absorption of the 21.532 keV γ-rays by bismuth necessitated the use of thin absorbers and all the samples used contained 3 mg cm^{-2} of europium. For comparison purposes, spectra were also collected from an absorber of dried C–Eu_2O_3 with the same thickness. Quadrupole splitting parameters were obtained by the least-squares fitting of the appropriate Hamiltonian using the thin-absorber approximation and using values for the quadrupole moments of $Q_g = +1.14 \times 10^{-28}$ m^2 and $Q_e/Q_g = +1.31$.

Results and Discussion

The X-ray diffraction pattern from the sample with $x = 0.3$ prepared at ambient pressure could be indexed in a face-centered cubic unit cell with a lattice parameter $a_0 = 5.518(1)$ Å, consistent with the adoption of an anion-deficient fluorite structure. The pattern from the sample with $x = 0.2$ could be indexed in the rhombohedral space group $R\bar{3}m$ with $a_0 = 3.974(2)$, $c_0 = 27.375(9)$ Å (hexagonal setting), apparently the same rhombohedral structure reported previously for low values of x in the solid solution $(Bi_2O_3)_{1-x}(Sm_2O_3)_x$ (*2*). These results are consistent with our previous suggestion (*4*) that there is a critical value of the average cation radius in $(Bi_2O_3)_{1-x}(M_2O_3)_x$ solid solutions, below which the fluorite structure is unstable with respect to the rhombohedral phase. The $x = 0.3$ composition in the Bi_2O_3/Eu_2O_3 solid solution transformed from the cubic to the rhombohedral structure after treatment at 4 GPa and 873 K. The unit cell parameters of the latter phase were $a_0 = 3.958(2)$, $c_0 = 27.32(1)$, the 2% reduction in the volume per formula unit confirming that the rhombohedral phase has a more densely packed structure, as suggested by our previous high-pressure studies (*4*) and the evolution of the structure of $(Bi_2O_3)_{0.7}(Sm_2O_3)_{0.3}$ with increasing temperature (*2*). A second aliquot of the $x = 0.3$ sample showed a different phase transition when treated at 1073 K and 4 GPa, the product being apparently isostructural with the phase labeled "*M*" in the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ system. We are still unable to index the X-ray diffraction pattern of this phase, but we believe that the symmetry is monoclinic or lower. It is interesting to note that the high-pressure phases reported here for $(Bi_2O_3)_{1-x}(Eu_2O_3)_x$ are not those that would have been expected to form under the same conditions for the Y and Er-containing solid solutions. The pressure-dependence of the structure of these compounds is clearly sensitive to the rare-earth element involved, in a way which cannot be explained using the limited amount of data presently available.

The room temperature Mössbauer spectra of the three samples having $x = 0.3$ are plotted in Fig. 2. The spectrum of C–Eu_2O_3 is also plotted for comparison. All three of the solid solutions appear to show a single resonance without any obvious hyperfine interactions, but attempts to curve-fit the spectra using only one Lorentzian-shaped line were not very satisfactory. The χ^2 values per degree of freedom (χ^2/d) were generally too large. The linewidths, Γ, and isomer shifts, δ, obtained using this simple model are listed in Table I. All the linewidths are substantially broader than the natural linewidth of 1.31 mm s^{-1}, and there is clear evidence that the line profiles are not accurately Lorentzian, although the lineshape for the cubic sample was almost symmetrical such that a Lorentzian line appeared to be a good approximation. The value of δ measured for C–Eu_2O_3 agrees well with previous work (*15*). The poor agreement between the observed and calculated spectra implies that either a second Eu site or a quadrupole interaction should be included in the data analysis. In view of the relative insensitivity of δ to coordina-

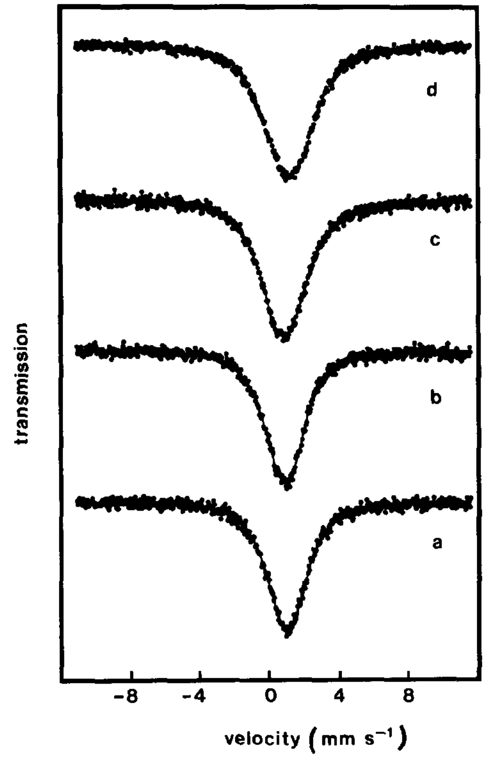

FIG. 2. The ^{151}Eu Mössbauer spectra at room temperature for the three forms of $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$: (a) cubic, (b) rhombohedral, (c) phase *M*; and (d) *C*-Eu_2O_3. The theoretical quadrupole curve fit is drawn for (a)–(c) only and follows the subtle distortion of the lineshape to high accuracy.

tion geometry in ^{151}Eu Mössbauer spectroscopy and the nonspherical cation environments which will inevitably be found in these anion-deficient solid solutions, it is more appropriate and realistic to introduce a quadrupole interaction than a second Eu site; the data are not of sufficient quality to justify the use of both.

A more sophisticated analysis technique including transmission integral calculations was attempted, but the results were not sufficiently significant to warrant their inclusion. In this manner we avoided the risk of overinterpretation.

The origin and nature of the quadrupole interaction in ^{151}Eu Mössbauer spectroscopy is complex and has been discussed in detail elsewhere (*16*, *17*). In a powder sample the observable parameters are the quadrupole coupling constant e^2qQ_g and the asymmetry parameter η. The effect of the interaction is usually to produce line broadening and asymmetry in the observed resonance; estimating the true extent of these effects for a particular sample is made difficult by the fact that the source matrix, SmF_3, is not a cubic material and it is therefore likely that the source lineshape is itself slightly asymmetric. The Mössbauer spectra of the three $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ phases were modeled with the inclusion of quadrupole effects at one unique Eu site, and the parameters obtained are given in Table II. The χ^2 values were now more reasonable, and the observed absorption profiles were well reproduced. A correction for the thickness of the absorber was not necessary. The refined values of e^2qQ_g, and particularly η, are sensitive to the source lineshape, and may have larger errors associated with them than the statistical values quoted in Table II. The spectrum of rhombohedral $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ shows a linewidth similar to that of the cubic form, but with a significant shift to lower velocity. Phase *M* also shows a lower shift, but with a broader line signifying a larger quadrupole splitting, which, more significantly, has the opposite sign of e^2qQ_g.

TABLE I

MÖSSBAUER PARAMETERS AT 290 K FOR A SINGLE LORENTZIAN LINE FIT

Compound	δ (mm s^{-1})	Γ (mm s^{-1})	χ^2/d
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (cubic)	0.86(1)	2.57(3)	1.00
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (rhombohedral)	0.76(1)	2.52(3)	1.30
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (phase *M*)	0.74(1)	2.97(3)	1.38
C-Eu_2O_3	1.03(7)	3.24(3)	1.63

TABLE II

MÖSSBAUER PARAMETERS AT 290 K FOR A SINGLE QUADRUPOLE FIT

Compound	δ (mm s^{-1})	Γ (mm s^{-1})	e^2qQ_g (mm s^{-1})	η	χ^2/d
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (cubic)	0.844(10)	2.08(7)	+4.7(3)	0.74(12)	0.90
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (rhombohedral)	0.719(10)	1.88(5)	+5.5(2)	0.63(8)	1.03
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ (phase *M*)	0.765(9)	2.25(6)	−6.1(2)	0.70(7)	1.09

The results reported above indicate that there are differences between the Eu environment in the different phases of the solid solution, but the resolution of the ^{151}Eu Mössbauer experiment is, in general, too low to justify a more detailed discussion of the results. However, the data for the cubic phase of $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ can be usefully compared with those collected on C–Eu_2O_3. The Mössbauer linewidth of the latter compound is the largest of all the materials studied here, and it was considered that this could be due to the presence of the two distinct Eu sites (Fig. 1).

The exact structural parameters for C–Eu_2O_3 are unknown, but they are available for the isostructural compound Er_2O_3 (*18*). The electric field gradient parameters were computed for both the cation sites in the C-type structure using the structural parameters for Er_2O_3 and following the method applied earlier to $EuFeO_3$ (*16*). The converged summation of the lattice term was obtained for a sphere of 50 Å radius containing over 37,000 atoms, and both the lattice and valence terms were calculated. For the 8*b* sites (space group $Ia\bar{3}$) on the threefold axis (Fig. 1a) the values obtained at 290 K were $e^2qQ_g = +17.7$ mm s^{-1}, $\eta = 0$; for the 24*d* sites (Fig. 1b) $e^2qQ_g = -6.7$ mm s^{-1}, $\eta = 0.80$. In view of the fact that the quadrupole coupling constants have opposite signs, largely due to the different distributions of nearest-neighbor vacancies, it is likely that the Mössbauer absorption line will be relatively broad. The fact that cubic $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ has a Mössbauer linewidth much narrower than that of C–Eu_2O_3 is thus very significant, clearly showing a much smaller range of environments to be present in the solid solution. This is at first surprising because the disorder between Bi and Eu on the cation sublattice would be expected to broaden the line, but the narrowing can be understood if we assume that the anion vacancies in this material order in such a way as to create a single, reasonably well-defined local environment for the Eu atoms in the solid solution. The results of the Mössbauer experiments are thus consistent with those from neutron scattering (*6*), EXAFS (*10*), and NMR (*11*) experiments, which suggested a well-ordered local environment around the dopant cation. The previous work led to the suggestion that ⟨111⟩ vacancy ordering occurs around the rare-earth cation and this would be consistent with the positive sign of the coupling constant found here for the 30% Eu-doped material. The lowering of the local symmetry will allow η to be nonzero at this site. The magnitude of the calculated value of e^2qQ_g at the 8*b* site in Er_2O_3 is highly sensitive to small (ca. 0.1 Å) anion displacements, although the sign always remains positive. However, although we believe that our Mössbauer data provide strong evidence for local anion ordering around the Eu^{3+} ions, we do not consider that we have shown convincingly that the ordered environment is that of Fig. 1a.

The decrease in linewidth observed following the cubic to rhombohedral phase transition suggests that the environment of the Eu ions is even more uniform in the denser phase. The observation of a positive quadrupole coupling constant in both samples is consistent with our previous suggestion, prompted by the results of neutron scattering experiments (*6*, *7*), that the anion vacancy ordering in the cubic phase involves the formation of small microdomains of the rhombohedral phase. However, the marked change in isomer shift indicates that the environment about the cation is significantly different in the two forms. The local ordering in phase *M* appears to be quite different, as evidenced by the change in sign of the quadrupole parameter.

In an attempt to ascertain whether the oxygen migration could affect the Mössbauer spectrum of the cubic phase, the latter was recorded as a function of temperature from 78 to 773 K. The recoilless fraction decreases with temperature rise, so that the absorption decreases by nearly an order of magnitude in that range. No significant change in the absorption linewidth or lineshape was observed apart from the normal second-order Doppler shift. The temperatures above room temperature were accessed by placing the sample in an evacuated furnace, and after several days at 773 K the sample was found to have lost oxygen with the production of metallic bismuth.

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