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On the Lattice Parameter of Some Sesquioxides with the Fluorite Structure

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Lattice constants for hypothetical room-temperature fluorite forms of Bi_2O_3 and rare-earth oxides are determined by application of Vegard's rule to fluorite solid solutions. Analysis shows that there are at least two different fluorite structures for sesquioxides, thereby explaining anomalous thermal expansivity data in the literature. A general equation for the prediction of room-temperature lattice constants for fluorite sesquioxide solid solutions is presented. © 1990 Academic Press, Inc.

1. Introduction

The δ-phase of Bi_2O_3, which is the stable form in the temperature range 1002–1097 K (*1*), has the fluorite structure and consequently one-fourth of the anion sites are unoccupied at any particular time. δ-Bi_2O_3 has, therefore, the remarkable high ionic conductivity of ~ 1 S · cm^{-1} (*2*) making it among the best oxide conductors known. There has been considerable interest in stabilizing the fluorite structure at lower temperatures (*3–22*) by the addition of divalent, trivalent, pentavalent, and hexavalent ions, but these solid solutions generally have a lower conductivity then the pure δ-phase (*9*).

In the course of our study of Bi_2O_3, using both static lattice (*23–26*) and dynamic (*27–30*) simulation techniques, it became necessary to know the lattice parameter of δ-Bi_2O_3 as a function of temperature. The experimental data display some inconsistencies; for example, Gattow and Schröder (*31*) report a value for the thermal expansivity constant, β, of 4.36×10^{-5} K^{-1}, whereas Levin and Roth (*32*) found $\beta = 2.4 \times 10^{-5}$ K^{-1}, and Taylor (*33*) reports a similar value of $\beta = 2.52 \times 10^{-5}$ K^{-1}. These data were all based on high-temperature studies in the narrow range of approximately 100 K where the δ-phase is stable. We therefore set out to determine the lattice parameter $a(T)$ as accurately as possible using crystallographic data on mixed oxides with the fluorite structure. Such data exist mainly at room temperature, but if we could determine the lattice parameter of the metastable δ-Bi_2O_3 at room temperature precisely, this could be used to fix $a(T)$ and the expansiv-

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ity of δ-Bi_2O_3 at higher temperatures. Moreover, where Vegard's rule is well obeyed it could also yield lattice constants for the hypothetical fluorite phase of pure rare-earth oxides. Although this phase is not observed experimentally such data would be of considerable value in predicting the lattice parameter of binary sesquioxide solutions for which the fluorite structure is stable.

In the course of this study it becomes clear that there are at least two structures for "fluorite" sesquioxides and this accounts for several apparently anomalous experimental observations.

2. Data Analysis

In this paper literature reports of the dependence of the lattice parameter of $(M_cO_d)_{1-x}(M'_eO_f)_x$ (as a function of x), where M_cO_d was generally (*3, 5, 6, 9, 11, 12, 15–19, 22*), but not invariably (*34, 35*), Bi_2O_3, are analyzed. According to Vegard's law, one expects a linear relationship and this was generally found to be so provided that no phase changes occurred. The best fit to $a(x)$ was determined either graphically, from photographic enlargements of the original authors' graphs, or, where possible, by using a linear least-squares program. For some data sets it proved necessary to eliminate some data points which clearly either involved some experimental error or a phase change. The lattice parameters of the metastable fluorite structures of M_cO_d and M'_eO_f at room temperature (i.e., $x = 0$ and $x = 1$) were then determined by extrapolation for those systems obeying Vegard's rule and are summarized in Table I.

3. Discussion

3.1 Lattice Parameter of δ-Bi_2O_3 at 298 K

The six systems $(Bi_2O_3)_{1-x}(M'_eO_f)_x$ with M' = Gd, Dy, Er, Yb, Nb, and V obey Vegard's rule. The graphical analysis employed for solid solutions with Gd_2O_3 (i) and (ii), Dy_2O_3 (i), and Er_2O_3 (i) (Table I) is quite reliable and the uncertainties in the lattice parameters of the pure components have been estimated quite generously. Of these six systems the following seven data sets (identified by the dopant oxide) are in almost perfect agreement in their predicted values for $a(Bi_2O_3)$: Er_2O_3 (i) and (ii), Gd_2O_3 (i) and (ii), Dy_2O_3 (i), Nb_2O_5 (i), and V_2O_5. Estimates based on Nb_2O_5 (ii) and Yb_2O_3 show the greatest deviations while Y_2O_3 is known to obey Vegard's rule rather poorly. Excluding these last three values the average value for a is

$$\langle a(Bi_2O_3) = 5.568 \pm 0.002 \text{ Å}\rangle \quad (1)$$

The agreement between the extrapolated values in Table 1 obtained from the work of

TABLE I

LATTICE PARAMETERS OF THE TWO COMPONENTS 1 = M_cO_d AND 2 = M'_eO_f (OF $(M_cO_d)_{1-x}(M'_eO_f)_x$ SOLID SOLUTIONS) DETERMINED FROM EXPERIMENTAL DATA ON THE MIXED OXIDES USING VEGARD'S RULE

Exptl. Ref.	1 = M_cO_d	2 = M'_eO_f	a_1 (Å)	a_2 (Å)	a_3 ($x = 0.5$) (Å)
(*3*)	Bi_2O_3	Gd_2O_3 (i)	5.568 ± 0.001[a,q]	5.375 ± 0.001[a]	5.472 ± 0.001[b]
(*6*)	Bi_2O_3	Gd_2O_3 (ii)	5.566 ± 0.002[a,q]	5.375 ± 0.002[a]	5.472 ± 0.004[a]
(*10*)	Bi_2O_3	Gd_2O_3 (iii)	(5.568)[f,k]	5.356[f]	5.462[c]
This work	Bi_2O_3	Gd_2O_3 —	(5.568)[k]	5.376 ± 0.075	5.472 ± 0.039
(*12*)	Bi_2O_3	Dy_2O_3 (i)	5.567 ± 0.001[a,q]	5.294 ± 0.002[a]	5.430 ± 0.002[a]
(*10*)	Bi_2O_3	Dy_2O_3 (ii)	(5.568)[f,k]	5.316[f]	5.442[c]
This work	Bi_2O_3	Dy_2O_3 —	(5.568)[k]	5.290 ± 0.077[r]	5.429 ± 0.040[r]

TABLE I—*Continued*

Exptl. Ref.	$1 = M_cO_d$	$2 = M'_eO_f$	a_1 (Å)	a_2 (Å)	a_3 ($x = 0.5$) (Å)
(*11*)	Bi_2O_3	Er_2O_3 (i)	$5.569 \pm 0.002^{a,q}$	5.225 ± 0.003^{a}	5.398 ± 0.001^{a}
(*16*)	Bi_2O_3	Er_2O_3 (ii)	$5.568 \pm 0.007^{d,e,q}$	$5.209 \pm 0.015^{d,e}$	5.389 ± 0.011^{b}
(*10*)	Bi_2O_3	Er_2O_3 (iii)	$(5.568)^{f,k}$	5.224^{f}	5.396^{c}
This work	Bi_2O_3	Er_2O_3 —	$(5.568)^{h}$	5.205 ± 0.079^{r}	5.387 ± 0.041^{r}
(*34*)	U_3O_8	Er_2O_3 (i)	$5.380^{a} \pm 0.001^{a}$	5.265 ± 0.001^{a}	—
(*34*)	U_3O_8	Er_2O_3 (ii)	5.3799 ± 0.0005^{g}	5.2648 ± 0.0006^{g}	—
(*35*)	ZrO_2	Er_2O_3 (iii)	5.1413 ± 0.0002^{g}	5.270 ± 0.001^{g}	—
(*16*)	Bi_2O_3	Yb_2O_3 (i)	5.558 ± 0.007^{d}	5.160 ± 0.019^{d}	5.359 ± 0.013^{b}
(*16*)	Bi_2O_3	Yb_2O_3 (ii)	$5.568 \pm 0.012^{d,h}$	$5.138 \pm 0.028^{d,h}$	5.353 ± 0.020^{b}
(*16*)	Bi_2O_3	Yb_2O_3 (iii)	$5.567 \pm 0.003^{d,i}$	$5.139 \pm 0.009^{d,i}$	5.353 ± 0.006^{b}
This work	Bi_2O_3	Yb_2O_3 —	$(5.568)^{k}$	5.150 ± 0.081^{r}	5.359 ± 0.042^{r}
(*15*)	Bi_2O_3	Y_2O_3 (i)	5.545 ± 0.011^{d}	5.304 ± 0.021^{d}	5.425 ± 0.016
(*15*)	Bi_2O_3	Y_2O_3 (ii)	5.568^{j}	5.266^{j}	5.417^{b}
(*21*)	Bi_2O_3	Y_2O_3 (iii)	$(5.568)^{m,k}$	5.280^{m}	5.424^{b}
(*15*)	Bi_2O_3	Y_2O_3 (iv)	$(5.568)^{k}$	5.236^{l}	5.402^{b}
(*5*)	Bi_2O_3	Y_2O_3 (v)	5.577 ± 0.002^{a}	—	—
(*10*)	Bi_2O_3	Y_2O_3 (vi)	$(5.568)^{f,k}$	5.288^{f}	5.428^{c}
(*15, 21*)	Bi_2O_3	Y_2O_3 (vii)	5.578 ± 0.004^{n}	5.249 ± 0.008^{n}	$5.413 \pm 0.006^{b,n}$
This work	Bi_2O_3	Y_2O_3 —	$(5.568)^{k}$	5.247 ± 0.078^{r}	$5.408 \pm 0.040^{b,r}$
(*10*)	Bi_2O_3	Sm_2O_3	$(5.568)^{f,k}$	5.504^{f}	5.536^{c}
This work	Bi_2O_3	Sm_2O_3	$(5.568)^{k}$	5.465 ± 0.073^{r}	$5.517 \pm 0.038^{b,r}$
(*10*)	Bi_2O_3	Eu_2O_3	$(5.568)^{f,k}$	5.398^{f}	5.483^{c}
This work	Bi_2O_3	Eu_2O_3	$(5.568)^{k}$	5.406 ± 0.074^{r}	$5.487 \pm 0.038^{b,r}$
(*10*)	Bi_2O_3	Ho_2O_3	$(5.568)^{f,k}$	5.294^{f}	5.431^{c}
This work	Bi_2O_3	Ho_2O_3	$(5.568)^{k}$	5.261 ± 0.078^{r}	$5.415 \pm 0.040^{b,r}$
(*18*)	Bi_2O_3	V_2O_5	$5.567 \pm 0.004^{a,q}$	—	—
(*19*)	Bi_2O_3	MoO_3	$5.565 \pm 0.004^{a,p}$	—	—
(*19*)	Bi_2O_3	WO_3	$5.528 \pm 0.004^{a,p}$	—	—
(*9*)	Bi_2O_3	Nb_2O_5 (i)	$5.569 \pm 0.005^{a,q}$	—	—
(*22*)	Bi_2O_3	Nb_2O_5 (ii)	5.575 ± 0.001	—	—
(*17*)	Bi_2O_3	SiO_2 (i)	$5.551 \pm 0.001^{c,p}$	—	—
(*38*)	Bi_2O_3	SiO_2 (ii)	$5.525^{c,o}$	—	—

[a] Lattice constants and estimated uncertainty from graphical analysis.

[b] Calculated by interpolation from a_1 and a_2.

[c] Direct determination by experiment.

[d] Lattice constants and standard deviations determined by least-squares fitting.

[e] If the point $a = 5.568$ Å at $x = 0$ is included along with the three points, the standard deviation is reduced to 0.004 Å. The value for $a(Er_2O_3)$ is almost unaffected (5.208 Å).

[f] a_2 calculated using 5.568 Å for a_1 (this work) and data of Nasonova *et al.* (*10*).

[g] Least-squares fitting of points obtained by graphical analysis.

[h] With point at $x = 0.2$ omitted in the least-squares analysis.

[i] Point $a = 5.568$ Å for Bi_2O_3 added to "anchor" the plot.

[j] Same as footnote *d* but with the point at $x = 0.27$ omitted in the least-squares analysis.

[k] Values in parentheses mean that value assumed in analysis.

[l] Using values for $x = 0$, $x = 0.27$ only (Y_2O_3 in ordered form).

[m] Using $x = 0$ (this work) and $x = 0.25$ from Infanté *et al.* (*21*).

[n] Data of Battle *et al.* (*15*) but with the 25% Y_2O_3 point of Infanté *et al.* (*21*) used in place of the apparently deviant data point at 27% Y_2O_3.

[o] Quenched Bi_2O_3 probably contaminated with SiO_2 (see (*32*)).

[p] System does not obey Vegard's rule.

[q] Used in the determination of a (298 K) for δ-Bi_2O_3.

[r] Calculated from Eq. (2).

nine studies by six different authors on six different systems is striking and supports our confidence in the procedure and in the results obtained. The agreement of the result obtained from Er_2O_3 (ii) with the other values for a may perhaps be considered fortuitous, since only three data points were used. The same might be said of the V_2O_5 values. However, even the most divergent values of 5.558 ± 0.007 Å from the Yb_2O_3 data or 5.575 ± 0.001 Å for Nb_2O_5 (ii) differ from the average value given in Eq. (1) above by only 0.01 Å or less, which is smaller than the differences between directly determined values at high temperatures.

The systems $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ ((ii) in Table I) and $(Bi_2O_3)_{1-x}(MoO_3)_x$ do not obey Vegard's rule perfectly yet nevertheless yield values for a, in good agreement with Eq. (1). Y_2O_3-doped systems are well known to deviate somewhat from Vegard's rule, e.g., CeO_2–Y_2O_3 (*36*). Takahashi *et al.* (*5*) confirmed the presence of a deviation from Vegard's rule in the Bi_2O_3–Y_2O_3 system, even at low dopant concentrations. However, this deviation was found to be very slight, and linear extrapolation by us yielded an estimate for the lattice constant of pure δ-Bi_2O_3 of 5.577 ± 0.002 Å.[1] This value is probably a slight overestimate as it ignores the negative curvature. By contrast, the data of Battle *et al.* ((i) in Table I) (*15*) yields the rather low value of 5.545 ± 0.011 Å for pure δ-Bi_2O_3. In light of this room temperature lattice constant it would appear that Battle *et al.*'s lattice constant for $(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$ is too low (Fig. 1, Table II) as it shows the greatest deviation from linearity. This deviation is much greater than that reported by Takahashi *et al.* (*5*). Moreover, the lattice constant determined by Infanté *et al.* (*21*) for $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ deviates much less from Vegard's rule (Fig. 1, Table II). Removal of the apparently erroneous point for 27% doped Bi_2O_3 from the data of Battle *et al.* yields an estimate for pure δ-Bi_2O_3 of 5.568 Å (from the remaining two points), in perfect agreement with the value obtained above from solid solutions obeying Vegard's rule. Alternatively, if we replace the lattice constant for 27% doped Bi_2O_3 by that of 5.496 Å for 25% yttria doped Bi_2O_3 deter-

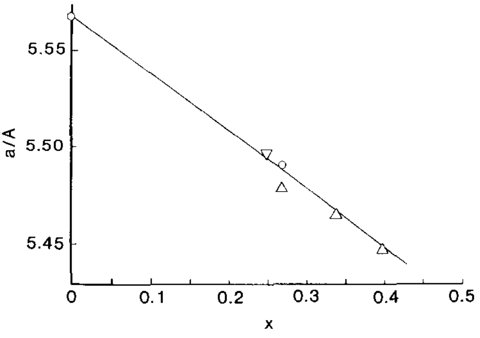

FIG. 1. Lattice parameter a of $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ as a function of x; ○, this work; △, Battle *et al.* (*15*); ▽, Infanté *et al.* (*21*). See Table I for details.

TABLE II

LATTICE PARAMETER DATA ON $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ SOLID SOLUTIONS AT ROOM TEMPERATURE

Reference	x	a (Å)
(*15*)	0.27	5.4784
(*15*)	0.34	5.4650
(*15*)	0.40	5.4469
(*21*)	0.25	5.496
This work[a]	0.27	5.490
This work	0.00	5.568

[a] Determined by extrapolation of the $x = 0.25$ lattice parameter from reference (*21*). a ($x = 0$) was taken as 5.568 Å. See Fig. 1.

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[1] In Takahashi *et al.*'s study of the Bi_2O_3–Y_2O_3 system (*5*), the values for the lattice constant, a, were incorrectly annotated in Fig. 2, which depicted the lattice constant as a function of x. It was possible to calibrate the scale by reference to the work of Battle *et al.* (*15*).

mined by Infanté *et al.* (*21*), an estimated lattice constant for pure δ-Bi_2O_3 of 5.578 ± 0.004 Å is obtained. This latter value is in excellent agreement with that obtained above from the data of Takahashi *et al.* (*5*), which, as previously argued, is probably a slight overestimate.

An estimate of 5.565 ± 0.004 Å for room temperature Bi_2O_3 was obtained from the $(Bi_2O_3)_{1-x}(MoO_3)_x$ system by extrapolation of the line through the two data points at $x = 0.075$ and $x = 0.1$ (Table I). This result is also in agreement with that obtained from systems obeying Vegard's rule.

Other systems, however, yield values which differ greatly from 5.568 Å (Table I). The Bi_2O_3–WO_3 and Bi_2O_3–SiO_2 systems yield much smaller lattice constants for room-temperature Bi_2O_3, close to the values reported by Sillén (*37*) and Schumb and Rittner (*38*) (Table I). Thus while most evidence suggests a room-temperature lattice constant of 5.568 Å there is evidence of another structure with $a = 5.525$ Å.

3.2 Evidence for Phase Changes in Fluorite Bi_2O_3, Er_2O_3, and Y_2O_3

Conductivity plots for $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ (for $x = 0.2$ and $x = 0.25$) show a bend in the Arrhenius plot at approximately $T = 870$ K, T_B, corresponding to a change in the activation energy and pre-exponential terms (*11*). Similar knees in the conductivity plots have been reported for the Bi_2O_3–Y_2O_3 (*5*), Bi_2O_3–Dy_2O_3 (*12*), Bi_2O_3–Gd_2O_3 (*6*), and Bi_2O_3–Nb_2O_5 (*9*) systems. This change in the activation energy for oxygen migration reflects an order–disorder transition in the oxygen sublattice (*14*) and is associated with an expansion of the lattice constant from one fcc form to another. The lattice constant of $(Bi_2O_3)_{0.8}(Er_2O_3)_{0.2}$ has been measured as a function of temperature by Verkerk *et al.*, using neutron diffraction (*14*). From plots of the lattice parameter against temperature we calculate expansivities of 4.4×10^{-6} K^{-1} for $T < T_B$ and 3.8×10^{-5} K^{-1}, $T > T_B$, with a discontinuity in $a(T)$ at T_B associated with an expansion in a of 0.01 Å or 0.18%. Direct measurements gave expansions at T_B of 0.17% using neutron diffraction (*14*) and 0.15% from Guinier measurements (*11, 14*). However, crystals of $(Bi_2O_3)_{1-x}(Dy_2O_3)_x$ with $x = 0.25$–0.35 also show changes in slope of the conductivity plots which are not associated with measurable changes in unit cell volume (*12*). A lattice expansion from one fcc phase to another in the case of $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ is also observed but it is too small to be measured accurately (*11*). We conclude that a change in slope ("knee") in the Arrhenius conductivity curve is associated with a lowering in oxygen order with increasing temperature but that this does not necessarily result in an accurately measurable change in structure.

Extrapolation from the data of Verkerk *et al.* (*11*) for $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ gives an estimate for $a = 5.525$ Å for the metastable fcc Er_2O_3. Nasonova *et al.*'s (*10*) lattice constant for $Bi_2O_3 \cdot Er_2O_3$ in combination with the value for δ-Bi_2O_3 calculated in this work together yield yet another estimate for Er_2O_3 of 5.224 Å. From the data of Battle *et al.* (*16*) the slightly lower value of 5.209 Å is obtained, although the values agree within experimental error. However, the analysis of studies of $(U_3O_8)_{1-x}(Er_2O_3)_x$ (*34*) and $(ZrO_2)_{1-x}(Er_2O_3)_x$ (*35*) using Vegard's rule yield lattice constants of 5.265 and 5.270 Å for Er_2O_3, respectively (Table I). This suggests the existence of two metastable fcc phases for Er_2O_3 with lattice constants of 298 K of 5.225 and 5.265–5.270 Å. The larger lattice constant represents an expansion of 0.8% (0.765–0.861%, Table III) over the smaller lattice constant.

The Bi_2O_3–WO_3 system yields an estimate of $a = 5.525$ Å for pure δ-Bi_2O_3 (Table I). Studies by Sillén (*37*) and Schumb and Rittner (*38*) also yield lattice constants of 5.525 Å (Table I) for Bi_2O_3 (apparently contaminated by SiO_2 (*32, 38*). It would appear,

TABLE III

LATTICE CONSTANTS OF THE ORDERED AND DISORDERED FORMS OF HYPOTHETICAL ROOM-TEMPERATURE FLUORITE SESQUIOXIDES

Sesquioxide	Ordered lattice parameter	Disordered lattice parameter	% Expansion
Bi_2O_3	5.525	5.568	0.78
Er_2O_3	5.225	5.2675[a]	0.81
Y_2O_3	5.236 (iv)[b]	5.280 (iii)[b]	0.84

[a] Average of (i) and (iii) (see Table I).
[b] Notation refers to Table I.

therefore, that there are two Bi_2O_3 phases at room temperature. Sillén (*37*) reported ⟨111⟩ ordering of oxygen vacancies. This model was supported by an electron diffraction study by Zav'yalova and Imamov (*39*) of $Bi_2O_{2.7-2.8}$ (a = 5.45 Å). Darbyshire and Cooper (*40*), also using electron diffraction, reported a yet smaller lattice constant of 5.425 Å, but it may be presumed that this was due to oxygen deficiency. A comparison of calculated and observed X-ray diffraction patterns by Medernach and Snyder (*41*) appears to confirm the Sillén model. Thus there would appear to be some reasonable evidence for the existence of an ordered fcc phase with a ⟨111⟩ oxygen vacancy arrangement. The lower lattice constant pertains to the more ordered system. The disordered fcc phase with the larger unit cell (a = 5.568 Å) corresponds to an expansion of 0.78% over the phase with the smaller unit cell (a = 5.525 Å). This coincides exactly with the expansion accompanying the order–disorder transition between the two proposed phases postulated for fluorite Er_2O_3 above (Table III).

Verkerk *et al.* (*11*) report an anomalous expansion from one fcc form to another in the Bi_2O_3–Y_2O_3 system, although they found it too small to measure accurately. As was shown above (Section 3.1) the lattice constant for $(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$ of 5.4784 Å reported by Battle *et al.* (*15*) deviates too much from Vegard's rule. Using Infanté *et al.*'s (*21*) value for the lattice constant of $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ (Table II), and a = 5.568 Å for pure δ-Bi_2O_3, and neglecting small deviations from Vegard's rule, a "corrected" lattice constant of 5.490 Å is obtained for $(Bi_2O_3)_{0.73}(Y_2O_3)_{0.27}$, which corresponds to an expansion of 0.21%. For a 20% doped system the equivalent expansion would have been 0.16% which is remarkably close to the order–disorder expansion observed for $(Bi_2O_3)_{0.8}(Er_2O_3)_{0.2}$ of 0.15–0.17% (*14*). The corresponding expansion for pure Y_2O_3 is 0.84% which matches almost exactly the order–disorder transition expansion calculated for the pure, metastable, fluorite phases of both Er_2O_3 and Bi_2O_3 (Table III). It seems likely therefore that the 27% yttria-doped Bi_2O_3 studied by Battle *et al.* (*15*) had undergone a disorder–order transition (in its Y_2O_3 component) and had contracted accordingly, whereas the 34 and 40% Y_2O_3 samples retained the disordered structure.

3.3 Ordered and Disordered Fluorite Phases

In all three substances Bi_2O_3, Er_2O_3, and Y_2O_3, there is clear evidence of the existence of at least two different phases, namely a more-ordered phase with a smaller lattice constant and a less-ordered phase with a larger lattice constant. There is an expansion of 0.8% associated with the transition from the ordered to the disordered phase. Bi_2O_3 exhibits a strong preference for the disordered phase and in almost all binary solutions the lattice constant versus percentage dopant plots yielded extrapolated values corresponding to the larger room-temperature lattice constant of 5.568 Å. Only Si and W yielded the smaller lattice constant of 5.525 Å of the ordered system. The thermal expansivity calculated using the larger lattice constant differs little from the thermal expansivity reported by Taylor (*33*) or Levin and Roth (*32*) which were determined from high-temperature data based on a range of a little over 100 K (see Section 3.5 below). This strongly suggests that the O^{2-} sublattice structure in the larger, disordered, room-temperature phase differs little from the high-temperature phase.

By contrast, Y_2O_3 and Er_2O_3 adopt the ordered phases much more readily, existing in the fluorite form only in binary solution with other oxides. The "phase" change is observed as an expansion of approximately 0.2% in $(Bi_2O_3)_{1-x}(M_2O_3)_x$, where x lies in the range 0.2–0.25. The Bi_2O_3 component retains the disordered form while the M_2O_3 component can exist in either form. Considering the data of Battle *et al.* (*15*) we find that Y_2O_3 component prefers the disordered form, except at 27% Y_2O_3 where the more ordered form with a contracted lattice constant is found. Our analysis of the data of Infanté *et al.* (*21*) suggests that they have the disordered form for 25% Y_2O_3 (Table II, Fig. 1). Verkerk *et al.* (*11*) reported an anomalous expansion in the lattice constant so it would appear that they, like Battle *et al.* (*15*), had the contracted, more-ordered, form.

In solid solution with Bi_2O_3 the rare-earth oxides appear to prefer the ordered form as reflected by the high activation barrier to migration. Only in a relatively narrow concentration range, which varies from substance to substance but which is generally centered on 20–25% rare-earth content, is a knee observed in the conductivity versus temperature curve, reflecting the order–disorder transition. Where such a bend is not observed the activation energy determined shows that the ordered form is favored, having the larger energy barrier to migration (e.g., (*12*)). Thus at least for the rare-earth oxides the ordered form is the more favored. The Bi_2O_3 component retains the disordered form.

By contrast, a slight trace of Si may induce Bi_2O_3 to transform into the more ordered form. This would appear to be the form observed by Sillén (*37*). The existence of two fluorite forms in δ-Bi_2O_3 must be largely responsible for the existence of an extensive literature of apparently contradictory analyses; contrast for example the work of Sillén (*37*) with that of Gattow and Schröder (*31*).

There are a number of reports in the literature which have perhaps been suggesting different δ-phases for Bi_2O_3. All studies agree on an fcc arrangement for the Bi^{3+} sublattice and consequently any differences must lie in the O^{2-} sublattice. Tsubaki and Koto (*42*) point out that the phase into which δ-Bi_2O_3 transforms on cooling is influenced by the temperature before cooling and on the cooling rate. For example, metastable forms (β- and γ-) do not appear when the sample is cooled from above 1163 K which is well into the liquid state. Clearly, therefore, Bi_2O_3 possesses a memory which is likely to be expressed as order in the O^{2-} sublattice. Molecular dynamics calculations by us (*27*) also confirm the existence of metastable O^{2-} configurations. Harwig and Gerards (*2*) observed a sudden fall in conductivity in the 913–937 K region above the γ-phase. They interpreted the phenomenon as an ordering process in the defect fluorite structure.

The already existing literature reports combined with this analysis of lattice constants confirm the existence of at least two

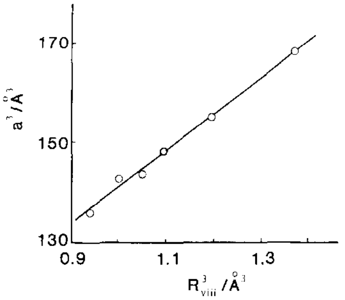

FIG. 2. Plot of a^3 versus R^3_{viii} for the ordered sesquioxides.

fluorite forms differing only in O^{2-} sublattice order.

3.4 The Lattice Parameters of Fluorite Sesquioxides at 298 K

The method adopted for establishing the lattice constant of metastable δ-Bi_2O_3 at room temperature also yields the lattice constants of the metastable fluorite phases for a number of other metal oxides. As these oxides do not adopt the fluorite structure at room temperature, the accuracy of these results cannot be checked directly by experiment. However, an indirect check exists, namely that of examining the linear dependence of a^3 on the cube of the ionic radii of the cations. Ionic radii, R, have been tabulated by Shannon and Prewitt (43) and were later updated by Shannon (*44*) using a modified procedure. R, however, depends on the coordination number and it is not clear whether the cations in the fluorite structure should be considered as 6-coordinate or 8-coordinate. Each cation is surrounded by eight lattice sites, but if the 25% vacancies are ordered along ⟨111⟩ (the Sillén structure for δ-Bi_2O_3), then the time- and space-averaged environment of each metal is 6-coordinate although the symmetry remains characteristic of an 8-coordinate environment. Statistically, the fit is found to be slightly better for R^2_{viii}. A plot of a^3 against R^3_{viii} is shown in Fig. 2.

It is clear from Table I that for certain oxides there are many candidate choices for the lattice parameter. The ionic radii employed were taken from Shannon and Prewitt (*43*). The correlation with the updated data of Shannon (*44*) proved significantly poorer and strong deviations from linearity were observed. Since the purpose of this fitting is to provide a simple means of predicting the lattice constants of sesquioxide solid solutions, we therefore use the original data of Shannon and Prewitt (*43*) for which the linear correlation of a^3 with R^3 is excellent. In our earlier determination of the room-temperature lattice constant of Bi_2O_3 four rare-earth oxides plus V_2O_5 were employed. Here we use the same four rare-earth oxides, together with Y_2O_3 and Bi_2O_3, to derive a general equation for the prediction of fluorite sesquioxide lattice parameters.

For Gd_2O_3 estimates (i) and (ii) (Table I) are in perfect agreement. Only the lattice parameter estimated from the data to Nasonova *et al.* (iii), for which the quality of data is poorer, is in disagreement. Similarly for Dy_2O_3, estimate (i) is considered to be the more reliable.

For Er_2O_3 we have two estimates for the smaller lattice constant, but the quality of data available to us is better for estimate (i) which we choose over (ii). For this particular case the estimate based on the data of Nasonova *et al.* (iii) is in agreement with (i). Yb_2O_3 is more of a problem. Estimates based on the raw data yield too low a lattice constant for Bi_2O_3 and would, therefore, potentially yield too high a lattice constant for Yb_2O_3 (i). By anchoring the lattice parameter dependence on percentage dopant by adding the estimate for room-temperature pure δ-Bi_2O_3, we get a new estimate for $a(Yb_2O_3)$ of 5.139 Å.

Only one lattice parameter in the case of Y_2O_3 corresponds to the ordered phase, namely that estimated from the 27% yttria-doped system (Battle *et al.* (*15*)) and the lattice constant of Bi_2O_3 (Y_2O_3 (iv), Table I). It is easily seen that the other larger lattice constants for Y_2O_3 would lie above the a^3 versus R^3_{viii} plot (Fig. 2), which reassuringly serves to justify our analysis of Y_2O_3 data. Finally, with Bi_2O_3 we use the lattice constant first estimated by Sillén (Table I, Bi_2O_3–SiO_2, (ii)). As can be readily seen it lies exactly on the a^3 versus R^3 plot. This strongly suggests that Sillén (*37*) examined the ordered form of Bi_2O_3 and explains the source of the disagreement with the work of many subsequent investigators. If the larger lattice constant of 5.568 Å of the disordered δ-phase is substituted the regression shows a poorer fit. Thus it would appear that the low lattice parameter, determined by Sillén, was simply due to a catalytic effect of the Si which promoted the transformation from the disordered to the ordered form. Were the low lattice parameters due to solid solution with a significant content it would be most unlikely that the lattice parameters would fit the plot so exactly. For the fluorite sesquioxides the room-temperature lattice constant of the more ordered form is given by

$$\langle a^3 = k \cdot R^3_{\text{viii}} + c \rangle \tag{2}$$

Values for k and c of 75.293 ± 3.051 and 65.735 ± 3.403 Å^3, respectively, were determined by least-squares regression ($R^2 = 99.3\%$). The lattice constants of the room-temperature binary solutions may be obtained by application of the above equation to generate the lattice constant of the fluorite rare-earth oxides followed by use of Vegard's rule to combine it with the lattice constant for room-temperature Bi_2O_3. If the rare-earth oxide has the disordered structure then the rare-earth lattice constant should be expanded by 0.8% prior to application of Vegard's rule. Calculated lattice parameters using this fit are given in Table I and the agreement with experimentally determined values is excellent. (The agreement is generally much better than the large standard deviation might indicate.)

In view of the good linear a^3 versus R^3 dependence one might suggest an equation of the form

$$a^3 = k \cdot R^3_{\text{eff}} + c \tag{3}$$

as a means of calculating the binary solution lattice parameters (where an effective radius, R_{eff}, is generated in a fashion analogous to Vegard's rule). However, it must be remembered that this linear relation is valid only for the ordered form of Bi_2O_3, whereas the solid binary solutions are usually between disordered Bi_2O_3 and ordered M_2O_3.

3.5 *Expansivity and Structures of δ-Bi_2O_3*

Experimental determinations of $a(T)$ for δ-Bi_2O_3 have been made only in a narrow temperature range around 1030 K, with the results shown in Table IV. The scatter in these data can be resolved if one recognizes that two fluorite structures are being observed in the δ-phase. Levin and Roth (*32*) have made sufficient measurements to determine the expansivity, β, of δ-Bi_2O_3 and find $\beta = 2.4 \pm 0.2 \times 10^{-5}$ K^{-1}. Recently Taylor (*33*) reported a similar value of $\beta = 2.52 \times 10^{-5}$ K^{-1}. Gattow and Schröder (*31*), however, reported the much greater expansivity of 4.36×10^{-5} K^{-1}. Our room-temperature lattice constant of 5.568 Å

TABLE IV

EXPERIMENTAL DETERMINATIONS OF THE LATTICE PARAMETER AND EXPANSIVITY OF δ-Bi_2O_3

Ref.	T (K)	a (Å)	β (10^{-5} K^{-1})	a (0 K) (Å)
(*15*)	1023	5.6485	1.98	5.536
(*1*)	1047	5.6595	2.18	5.532
(*45*)	1029	5.644	1.85	5.537
(*32*)	1032	5.66	2.26[a]	5.531

Note. The lattice parameters at 0 K are also shown.
[a] Levin and Roth (*32*) calculated a thermal expansivity of 2.4×10^{-5} K^{-1} using only their high-temperature data.

combined with Levin and Roth's (*32*) high-temperature lattice constant of 5.66 Å, yields a thermal expansivity of 2.26×10^{-5} K^{-1}. Thermal expansivities calculated using a variety of high-temperature lattice constants are displayed in Table IV. In all cases the thermal expansivity differs strongly from that of Gattow and Schröder (*31*). The data of Levin and Roth is that which agrees most closely with ours. Accordingly we use their high-temperature lattice constant and estimate a zero Kelvin lattice parameter for δ-Bi_2O_3 of 5.531 Å (Table IV).

We have already established the existence of two or more fluorite phases and it may be that Gattow and Schröder (*31*) measured the thermal expansivity of another fluorite phase. The probable cause of the disagreement with the data of Gattow and Schröder (*31*) is the substantially differing estimates of lattice constants in a relatively narrow temperature range. The variability in the lattice parameter for Bi_2O_3 may itself be a reflection of the existence of two or more fluorite forms.

4. Conclusions

This analysis of experimental data for the lattice parameter of fluorite-structured sesquioxides has provided the following information.

(a) Fluorite sesquioxides may exist in at least two forms, differing from each other in the degree of order in the O^{2-} sublattice. A phase change from the ordered to the disordered forms is associated with an expansion of 0.8%. The existence of at least two different fluorite forms resolves many apparently contradictory experimental reports in the literature.

(b) Vegard's rule is obeyed, except when phase changes occur between alternative fluorite forms.

(c) Bi_2O_3 favors the expanded or less-ordered fluorite forms. Its lattice parameter (metastable δ-Bi_2O_3) at room temperature is 5.568 ± 0.002 Å. This value is well-substantiated and may be used with confidence in analysis of future experimental data on the fluorite structured oxides (e.g., to "anchor" a plot of $a(x)$ and thus help to detect poor data or phase changes).

(d) The calculated lattice parameter of δ-Bi_2O_3 at room temperature based on (c) and Levin and Roth's (*32*) high-temperature data provides the best currently available estimates of $a(T)$. The thermal expansivity is found to be 2.26×10^{-5} K^{-1}.

(e) The lattice parameter of metastable δ-Bi_2O_3 at 0 K is 5.531 ± 0.002 Å, a value that is useful in the simulation of the δ-phase of Bi_2O_3 at 0 K.

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