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Structural Studies of Some Body-Centered Cubic Phases of Mixed Oxides Involving Bi_2O_3: The Structures of $Bi_{25}FeO_{40}$ and $Bi_{38}ZnO_{60}$

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The structures of the compounds initially reported to be $7 \cdot Bi_2O_3 \cdot ZnO$ and $96 \cdot Bi_2O_3 \cdot 4Fe_2O_3$, have been determined by X ray methods. Three dimensional, absorption corrected diffractometer data were used and atomic parameters were refined by least-squares procedures. The structures are isomorphous, cubic with $a = 10.194(3)$ and $10.179(3)$ Å, respectively, and space group I23. Each Bi^{3+} ion is surrounded by five oxygen atoms that form an incomplete octahedral arrangement with Bi–O distances ranging from 2.07–2.60 Å. The $6s^2$ inert electron pair completes the octahedron. The Bi^{3+} ions are vibrating anisotropically. Tetrahedral sites in the structures contain 61 and 46 electrons, respectively. These values are consistent with a statistical distribution of Zn^{2+} and Bi^{5+} ions or Fe^{3+} and Bi^{5+} ions on these sites. Molar ratios are derived that agree with the observed distributions of electron density and give rise to perfectly stoichiometric systems, devoid of cationic or anionic vacancies. The compositions studied correspond to $Bi^{3+}_{24}Bi^{5+}Fe^{3+}O_{40}$ and $Bi^{3+}_{36}Bi^{5+}_{2}ZnO_{60}$ and they are optical enantiomorphs.

It is proposed that a reduction in the percentage composition of Bi_2O_5 leads to metastable phases, in which all atomic positions remain fully occupied but some tetrahedral sites contain Bi^{3+} ions. The end product of the series is γ-Bi_2O_3 in which 50% of these sites contain Bi^{3+} and the remainder Bi^{5+} ions. We believe that γ-Bi_2O_3 is $Bi^{3+}_{25}Bi^{5+}O_{40}$.

Introduction

The structure of $Bi_{12}GeO_{20}$ has been determined by Abrahams, Jamieson, and Bernstein (*1*). This body-centered cubic cell is characteristic of a group of compounds formed between Bi_2O_3 and various other metal oxides. Aurivillius and Sillen (*2*) reported such compound formation with Al, Si, Fe, Zr, Ce, Tl, and Pb as the second metal (M), whereas this list has been greatly extended by Levin and Roth (*3*).

Quadrivalent metal oxides, MO_2, give stable phases approximated by the formula $Bi_{12}MO_{20}$, where the Bi:M ratio closely approaches 12:1, but may vary, Speranskaya and Arshakuni (*4*) formulated the germanium phase as $Bi_{14}GeO_{23}$ but the structural study by Abrahams et al. (*1*) proved the b.c.c. phase to be $Bi_{12}GeO_{20}$. The formula $Bi_{12}MO_{20}$ describes the *ideal* or stoichiometric species in which particular cationic and anionic sites in the b.c.c. cell are fully occupied. If the Bi:M ratio differs from 12:1, or if M is other than a quadrivalent metal, then the b.c.c. structure must contain fractionally occupied ionic sites or else accommodate the change in stoichiometry in some other way.

Metastable phases containing metal ions of large cationic radius can be prepared under the proper conditions of composition, grinding and heating schedules (*3*). The cell dimensions of the metastable phases are larger than those of the stable phases, the largest being that of γ-Bi_2O_3, which was first investigated by Sillen in 1937 (*5*). It is not possible for a substance with the composition Bi_2O_3 to have the structure $Bi_{12}MO_{20}$ (i.e., $B_{13}O_{20}$) and this problem has been discussed by numerous authors without being resolved.

We have examined the structures of two compounds initially reported to have the

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composition 7 Bi_2O_3ZnO (or $Bi_{12}Zn_{0.85}O_{18.85}$) and 96 $Bi_2O_3 \cdot 4Fe_2O_3$ (or $B_{12}Fe_{0.5}O_{18.75}$) in an attempt to resolve the structural aspects of the nonstoichiometry.

Experimental

The compounds were kindly provided by Dr. R. S. Roth. Preliminary treatment of the binary mixtures consisted of three cycles of grinding together calculated amounts of the starting materials, pressing the material in a mold, and then heating the disk at a temperature below the solidus. The final heat treatment involving heating the sample in a sealed platinum tube and in the case of 7 Bi_2O_3ZnO this was at 700°C for 107 hr while for 96 Bi_2O_3 $4Fe_2O_3$ the temperature was 700°C for 3 hr.

The smallest spheres that could be recovered from our Bond sphere grinder had average radii (r) of 0.0109 and 0.0085 cm for the respective compounds. The resulting μr values for both copper and molybdenum radiation calculated well outside the range given in the International Tables for X-Ray Crystallography, and therefore, for convenience, Cu K_α radiation was used to collect X ray data. There was no evidence of superlattice spots but, in case a slight change from cubic symmetry had occurred, due to an ordering of *defects*, one-eighth of the reciprocal lattice was recorded in each case. These data were collected using a Siemens A.E.D. computer controlled diffractometer, crystal orientation and angle calculation being accomplished using the method of Busing and Levy (*6*). Cell dimensions were determined from selected high-angle reflections and are listed below. These dimensions were also used in the refinement of the approximate *UB* matrix. Integrated intensities were obtained using a θ–2θ scan and the "4-value method" (*7*) of measurement.

Bi/Zn oxide	*Bi/Fe oxide*
$a = 10.1939(3)$	$a = 10.1789(3)$
$r = 0.0109$ cm	$r = 0.0085$ cm
$\rho c = 9.37$ $g \cdot cm^{-3}$	$\rho c = 9.32$ $g \cdot cm^{-3}$
$\mu r = 21.9$	$\mu r = 17.1$
*SG I*23	*SG I*23
Unit cell contents:	
$Bi_{25.333}Zn_{0.667}O_{40}$	$Bi_{25}FeO_{40}$

Intensities were corrected for instrumental drift, if any, using a periodically measured standard reflection as a reference. Background was assumed to vary linearly through the scan range for each reflection. Lorentz, polarization, and absorption corrections were applied using programs written in this laboratory.

Values of the absorption correction factor A^* were calculated for various values of θ by an analytical method involving a Gaussian approximation. A grid of 32 × 32 × 32 points was used and the values of A^* at θ values of 0° and 90° were found to agree to within 1% of the values calculated from the integral. Due to the very large values of A^* (maximum value 19500) it is probable that errors in absorption corrections arise not from the lack of an exact knowledge of A^*/θ relationships but rather from deviations in spherical shape.

Atomic scattering curves for bismuth, iron, zinc, and oxygen were taken from (*8*). Curves for neutral atoms were used and these values were corrected for the real part of the anomalous dispersion of copper K_α radiation by the respective atoms (*9*). All structure factor calculations utilized these $(f + \Delta f')$ curves together with the respective $\Delta f''$ values listed by Dauben and Templeton (*9*).

The Structure of 7 $Bi_2O_3 \cdot ZnO$

Solution and Refinement

Cell dimensions and structure amplitude distributions indicate that the structures of 7 $Bi_2O_3 \cdot ZnO$ and $Bi_{12}GeO_{20}$ are similar. $Bi_{12}GeO_{20}$ is cubic with space group I23 and lattice constant $a = 10.1455 \pm 0.0008$ Å. The cell contents are $Bi_{24}Ge_2O_{40}$ with one bismuth atom in a general 24*f* position with coordinates 0.8241, 0.6816, 0.9843.

To allow for the possibility that ionic vacancies, if any, are ordered—thereby destroying the I23 cubic symmetry of the stoichiometric species $A_{12}BO_{20}$—the structure of $7Bi_2O_3 \cdot ZnO$ was initiated in the orthorhombic system, using the appropriate space group

TABLE I

Final Atomic Coordinates for the Compound 7 $Bi_2O_3 \cdot ZnO$ Refined in the Space Group I222[a]

	Bi(1)	Bi(2)	Bi(3)	Zn	O(1)	O(2)	O(3)	O(4)	O(5)
x	0.82352(9)	0.98604(10)	0.68183(11)	0.0	0.3131(19)	0.3660(20)	0.2496(22)	0.0116(28)	0.1047(26)
y	0.68178(11)	0.82354(10)	0.98606(10)	0.0	0.3120(18)	0.2489(20)	0.0118(26)	0.3649(20)	0.1069(23)
z	0.98600(10)	0.68177(11)	0.82364(10)	0.0	0.3111(21)	0.0135(26)	0.3620(17)	0.2477(24)	0.1061(22)
$\beta(1,1)$	0.00154(7)	0.00226(8)	0.00461(9)	0.0073(8)	0.0049(19)	0.0037(19)	0.0049(23)	0.0053(24)	0.0052(28)
$\beta(2,2)$	0.00430(9)	0.00127(7)	0.00196(8)	0.0071(7)	0.0038(18)	0.0048(20)	0.0022(23)	0.0042(20)	0.0022(25)
$\beta(3,3)$	0.00214(8)	0.00457(9)	0.00147(7)	0.0082(8)	0.0069(21)	0.0046(24)	−0.0012(16)	0.0089(26)	0.0007(22)
$\beta(1,2)$	0.00093(9)	0.00001(8)	0.00105(8)	0.0	0.0018(16)	0.0007(15)	−0.0006(19)	−0.0019(19)	0.0005(18)
$\beta(1,3)$	−0.00002(8)	0.00106(8)	0.00101(9)	0.0	0.0022(18)	−0.0009(17)	−0.0009(14)	−0.0029(22)	0.0000(17)
$\beta(2,3)$	0.00096(8)	0.00104(8)	−0.00001(8)	0.0	0.0001(17)	−0.0020(19)	−0.0018(15)	0.0006(17)	0.0006(16)

[a] Standard deviations are given in parentheses and refer to the least significant digits. Site occupancies for all atoms do not significantly deviate from unity except Zn, which has a value of 2.16.

I222. Twenty-four Bi atoms were placed in three $8k$ positions of this space group with coordinates transformed from position $24f$ of I23. These parameters were refined using Busing, Martin, and Levy's ORFLS program and a difference Fourier synthesis was then computed. This function indicated the position of 40 oxygen atoms and showed significant electron density (peak height 30 e.$Å^{-3}$) on the $2a$ sites that have tetrahedral symmetry. These were tentatively treated as zinc atoms and least-squares refinement cycles were run in which site occupancies, positional, and anisotropic internal parameters were varied. The final R value is 0.033 and the results of the refinement are recorded on microfiche (Table I) together with other pertinent data.

Discussion

It was immediately apparent that the crystal system is cubic with space group I23. This was best illustrated by the equivalence of the positional parameters as well as the thermal matrix components of the three *unrelated* sets of bismuth atoms.

The site occupancy factors for bismuth and oxygen atoms did not deviate significantly from unity but the value for zinc, at position $2a$, converged to 2.16. When multiplied by the atomic number for zinc this value indicates that approximately 61 electrons are located at each $2a$ site. Therefore, there must be substitution by bismuth provided that no other metal atom other than zinc and bismuth are present in the crystal.

If each tetrahedral site is either fully occupied by a zinc atom ($f + \Delta f' = 28.3$e) or a bismuth atom ($f + \Delta f' = 78.4$e) and the composition is expressed $a Bi_2O_3 \cdot b ZnO$, then the molar ratio $a:b$ can be plotted against the electron population on each tetrahedral site. This is shown in Fig. 1 where 61 electrons correspond to a molar ratio of 18–19:1.[1] This ratio differs quite markedly from the

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[1] Order supplementary material from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, New York 10006. Remit in advance for each NAPS accession number \$1.50 for microfiche or —— for photocopies. Make checks payable to Microfiche Publications.

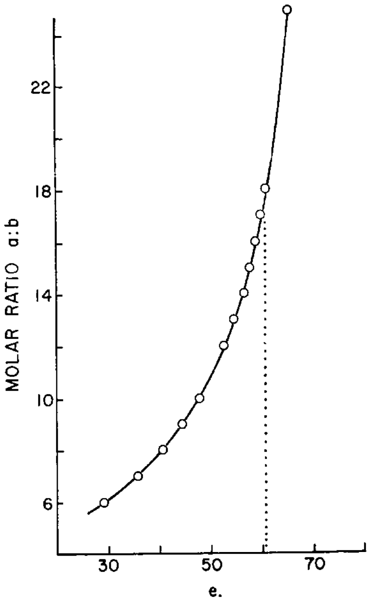

FIG. 1. A plot of molar ratio $a:b$ in the series $a\mathrm{Bi_2O_3}\cdot b\mathrm{ZnO}$ against electron population on each tetrahedral site $2a$.

original 7:1 value, but is not at variance with Roth's observation (*3*) that the original sample contained unreacted ZnO.

Composition and Stoichiometry

It seems likely that the bismuth substituting for zinc is $\mathrm{Bi^{5+}}$. As will be seen below, $\mathrm{Bi^{3+}}$ is an asymmetric ion containing a lone $6s^2$ electron pair and completes its coordination polyhedron with five other atoms to form an octahedron. In the case of oxygen atoms, the average distance is 2.34 Å. Therefore, a $\mathrm{Bi^{3+}}$ ion is too large and too asymmetric to occupy a position with site symmetry 23 and be surrounded by four oxygen atoms each at a distance of 1.89 Å.

Relevant deductions can be made if it is assumed that the b.c.c. phase contains $\mathrm{Bi^{5+}}$ ions. The stoichiometry is then determined by the values of a, b, and c in the formula $a\mathrm{Bi_2O_3}\cdot b\mathrm{Bi_2O_5}\cdot c\mathrm{ZnO}$ and the following equations hold

$2a + 2b + c = 26$ (number of cations in unit-cell)

$3a + 5b + c = 40$ (number of anions in unit-cell)

$a + b - Mc = 0$ (M is molar ratio).

The values of $2a$, $2b$, and c are the respective number of $\mathrm{Bi^{3+}}$, $\mathrm{Bi^{5+}}$, and $\mathrm{Zn^{2+}}$ ions in the

TABLE II

VALUES OF SOME COMPOSITIONAL PARAMETERS FOR THE SYSTEM $a\mathrm{Bi_2O_3}\cdot b\mathrm{Bi_2O_5}\cdot c\mathrm{ZnO}$ AS A FUNCTION OF THE MOLAR RATIO $(a + b)/c$

Molar ratio	Ions per unit-cell $\mathrm{Bi^{3+}}$	$\mathrm{Bi^{5+}}$	$\mathrm{Zn^{2+}}$	Small cations per unit-cell	ρ at each tetrahedral site	% of Bi oxidized
6:1	22.00	2.00	2.00	4.00	28.27	8.33
7:1	22.40	1.87	1.73	3.60	35.63	7.70
8:1	22.71	1.76	1.53	3.29	40.52	7.19
9:1	22.95	1.68	1.37	3.05	44.43	6.82
10:1	23.15	1.61	1.24	2.85	47.67	6.50
11:1						
12:1	23.42	1.52	1.06	2.56	52.49	6.09
13:1	23.56	1.48	0.96	2.44	54.40	5.91
14:1	23.67	1.44	0.90	2.34	56.60	5.73
15:1	23.74	1.42	0.84	2.26	57.42	5.64
16:1	23.82	1.39	0.79	2.18	58.70	5.51
17:1	23.90	1.36	0.74	2.10	59.67	5.38
18:1	23.96	1.34	0.70	2.04	60.78	5.29
19:1	24.00	1.333	0.667	2.00	61.67	5.18
25:1	24.24	1.25	0.51	1.76	65.51	4.90
γ-$\mathrm{Bi_2O_3}$	25.0	1	0	1.00	78.43	3.85

unit cell and these values are listed in Table II for a range of molar ratios.

As the molar ratio increases, the number of Bi^{3+} and Zn^{2+} ions per unit cell decreases. For example, at the supposed 7:1 ratio the number of small cations (i.e., Bi^{5+} and Zn^{2+}) is 3.60 and these may distribute as 2.0 over the tetrahedral sites and 1.6 over the 24 larger octahedral sites. This number gradually drops to 2.0 at the 19:1 molar ratio. At this ratio the number of small cations per unit cell is precisely 2.0 and this number equals the number of available tetrahedral sites. There are exactly 24 Bi^{3+} ions to occupy the octahedral positions, the anion lattice is complete and the electron population at the tetrahedral sites (62 electrons) equals the experimentally determined electron population (61 ± 1 electrons).

Absolute Configuration

In view of the fact that the composition and crystal symmetry of the Bi/Zn compound appear to differ so greatly from the initial values, the original X ray data were again corrected for absorption but with a μ value (2009.2 cm^{-1}) based on the composition $Bi^{3+}_{36}Bi^{5+}_{2}ZnO_{60}$. Equivalent structure amplitudes were averaged and the atomic parameters were refined by least-squares methods in the space group *I*23. The final parameters are listed in Table III. A microfiche of the 204 observed and calculated structure amplitudes has been deposited as a document with the ASIS National Auxilliary Publication Service.[2]

The final R value is 0.027 over all observed data and the value of $\omega R = [\sum (\omega^{1/2} \Delta F \text{meas})^2 / \sum (\omega^{1/2} F \text{ meas})]^{1/2}$, where the weight $\omega = 1/\sigma^2 F$ meas is 0.029. Replacement of each coordinate by $\bar{x}\bar{y}\bar{z}$ and subsequent refinement by least-squares until convergence, resulted in $\omega R = 0.031$. The value of R is 0.027.

The ratio $\omega R(xyz)/\omega R(\bar{x}\bar{y}\bar{z}) = 1.069$ exceeds Hamilton's R ratio (*10*) for the comparable one-dimensional hypothesis ($R_{1170.005} = 1.024$) and it seems likely that the coordinates listed in Table III describe the absolute configuration of the Bi/Zn compound.

An X ray Examination of the Compound 96 $Bi_2O_3 \cdot 4Fe_2O_3$

Introduction

To confirm the equilibrium composition and the structural features described above

TABLE III

FINAL ATOMIC PARAMETERS FOR THE COMPOUND $Bi_{38}ZnO_{60}$[a]

	Bi	Zn	O(1)	O(2)	O(3)
x	0.82352(8)	0.0	0.3117(49)	0.3661(14)	0.1069(58)
y	0.68178(8)	0.0	0.3117(49)	0.2496(15)	0.1069(58)
z	0.98603(7)	0.0	0.3117(49)	0.0118(19)	0.1069(58)
$\beta(1,1)$	0.00153(7)	0.0077(15)	0.0028(26)	0.0022(12)	0.0047(38)
$\beta(2,2)$	0.00440(8)	0.0077(15)	0.0028(26)	0.0039(14)	0.0047(38)
$\beta(3,3)$	0.00215(7)	0.0077(15)	0.0028(26)	0.0031(14)	0.0047(38)
$\beta(1,2)$	0.00091(7)	0.0	0.0016(39)	0.0007(11)	−0.0003(46)
$\beta(1,3)$	0.00001(6)	0.0	0.0016(39)	−0.0007(13)	−0.0003(46)
$\beta(2,3)$	0.00100(6)	0.0	0.0160(39)	−0.0009(15)	−0.0003(46)

[a] The site occupancy for zinc is 2.16 and for the remaining atoms these values are 1.0. The temperature factor has the form $\exp(-\beta_{11}h^2 + 2\beta_{12}hk + \ldots.)$.

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[2] Order supplementary material from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, New York 10006. Remit in advance for each NAPS accession number \$1.50 for microfiche or —— for photocopies. Make checks payable to Microfiche Publications.

for the compound containing the divalent metal zinc, another system was chosen in which the additional oxide was that of a trivalent metal, i.e., Fe_2O_3. The substance was kindly provided by Dr. R. S. Roth. The starting composition was 19 $Bi_2O_3 \cdot Fe_2O_3$ but after a final heat treatment of 700°C for 3 hr the specimen was found to contain traces of $BiFeO_3$, which effectively increases the percentage composition of Bi_2O_3 in the phase to be examined. The composition was estimated to be 96 $Bi_2O_3 \cdot 4Fe_2O_3$.

If the structure is postulated to contain bismuth atoms only on the octahedral sites, the composition must be expressed as $Bi_{24}FeO_{37.4}$. On the other hand if octahedral sites contain trivalent bismuth ions, if there is a complete anion lattice and if the smaller tetrahedral sites are fully occupied by trivalent iron or pentavelent bismuth ions, the equilibrium composition calculates to be $Bi^{3+}_{24}Bi^{5+}Fe^{3+}O_{40}$. In the former instance one would expect to find one-half of an iron atom ($f+\Delta f' = 24.87$), i.e., 12.4 electrons on each tetrahedral site, whereas if the theory developed above is correct, this number of electrons will be 51.65, i.e., $(24.87 + 78.4)/2$.

Solution, Refinement, and Absolute Configuration

The procedure adopted was precisely the same as that followed with the Bi/Zn compound. Bismuth and oxygen atoms were assigned the coordinates listed in Table I. Iron atoms were placed in position $2a$ and all structural parameters were refined in the space groups $I222$ using least-squares methods. The resulting occupancy factor for site $2a$ indicated that 46 (1) electrons were located there. The discrepancy between the expected electron population (51.56 e) on the tetrahedral site and the experimentally determined value (46 e) may be attributable to the extensive anomalous dispersion of Cu K_α radiation by iron atoms. The final R value was 0.036.

It was evident that $Bi^{3+}_{24}Bi^{5+}Fe^{3+}O_{40}$ has cubic symmetry. Therefore, the equivalent structure amplitudes were averaged and the atomic parameters were refined by least-squares methods in space group $I23$.

Absolute Configuration

The atomic coordinates taken from Table I converged to give a R value of 0.028 and a weighted R value of 0.029. Replacement of each coordinate set by $\bar{x}\bar{y}\bar{z}$, and subsequent refinement by least-squares until convergence, yielded values of $R = 0.021$ and $\omega R = 0.021$.

The ratio $\omega R(\bar{x}\bar{y}\bar{z})/\omega R(xyz) = 1.381$ considerably exceeds Hamilton's R ratio (*10*) for the comparable one-dimensional hypothesis ($R_{1170.005} = 1.024$) and leads to the conclusion that the information given by $\bar{x}\bar{y}\bar{z}$, i.e., in Table IV, is correct. This is the optical enantiomorph to the Bi/Zn compound.

TABLE IV

FINAL ATOMIC PARAMETERS FOR THE COMPOUND $Bi_{25}FeO_{40}$[a]

	Bi	Fe	O(1)	O(2)	O(3)
x	0.17635(5)	0.00	0.6885(31)	0.6346(10)	0.8926(32)
y	0.31796(5)	0.00	0.6885(31)	0.7521(10)	0.8926(32)
z	0.01409(5)	0.00	0.6885(31)	0.9887(14)	0.8926(32)
$\beta(1,1)$	0.00140(5)	0.0057(12)	0.0025(18)	0.0030(9)	0.0031(23)
$\beta(2,2)$	0.00370(6)	0.0057(12)	0.0025(18)	0.0030(9)	0.0031(23)
$\beta(3,3)$	0.00217(5)	0.0057(12)	0.0025(18)	0.0027(10)	0.0031(23)
$\beta(1,2)$	0.00071(4)	0.00	0.0009(26)	−0.0001(8)	−0.0008(25)
$\beta(1,2)$	−0.00011(4)	0.00	0.0009(26)	−0.0007(9)	−0.0008(25)
$\beta(2,3)$	0.00072(4)	0.00	0.0009(26)	−0.0008(10)	−0.0008(25)

[a] The site occupancy for iron is 1.85 and for the remaining atoms these values are 1.0.

Description of the Structures

The body-centered cubic structures derived above contain Bi^{3+} ions in octahedral coordination. The coordination polyhedron consists of an inert $6s^2$ electron pair and five oxygen atoms at distances listed in Table V. Within the limits of error these distances are the same for both compounds. The average Bi–O distance is 2.344 Å and this agrees with the average bond distance of 2.37 Å reported for other Bi^{3+} oxygen octahedra (*1*). The shortest Bi^{3+}–O distance of 2.068(15) Å occurs in the bond opposite the inert $6s^2$ electron pair. The remaining basal plane bond distances vary between 2.140 and 2.599 Å.

Two oxygen atoms from adjacent octahedra approach each Bi^{3+} ion from either side of the inert electron pair. The approach distances are 3.109 and 3.208 Å. The inert $6s^2$ electron pair of any Bi^{3+} ion points towards one other $6s^2$ electron pair from an adjacent Bi^{3+} ion. This Bi^{3+}–Bi^{3+} distance is 3.609 Å so that the electron pair can be considered to extend no further than 1.81 Å from the nucleus of the Bi^{3+} ion.

The 24 octahedra share corners to form a cage of $Bi_{24}O_{40}$ atoms and within this cage there are two tetrahedral sites. The resultant cage charge of 8 e is balanced by small cations that fully occupy the tetrahedral sites. In the case of the Bi/Fe compound there is one Bi^{5+} and one Fe^{3+} ion per cage. In the case of the Bi/Zn compound there are 1.333 Bi^{5+} and 0.667 Zn^{2+} ions distributed over the two sites in each cage. Whereas the octahedral polyhedra are distorted, the tetrahedra are perfectly regular with each metal–oxygen distance equal to 1.89 Å.

TABLE V

SELECTED BOND DISTANCES (Å)[a]

	Bi/Zn	*Bi/Fe*
$Bi(1)^1$–O(1)	2.220(037)	2.214(021)
$-O(2)^3$	2.251(018)	2.263(013)
$-O(2)^4$	2.594(018)	2.599(012)
$-O(2)^5$	2.072(015)	2.069(011)
$-O(2)^6$	3.113(017)	3.089(012)
$-O(2)^7$	3.206(017)	3.189(011)
$-O(3)^2$	2.581(037)	2.572(021)
$Bi(1)^8$	3.609(002)	3.602(001)
Zn(1)–O(3)	1.887(103)	1.894(057)

[a] Standard deviations, as calculated by ORFLS, are given in parentheses and refer to the least significant digits. Superscripts refer to the following symmetry transformations. 1: $x-\frac{1}{2}\ y-\frac{1}{2}\ z-\frac{1}{2}$. 2: $\frac{1}{2}-x\ \frac{1}{2}-y\ \frac{1}{2}+z$. 3: $y\ z\ x$. 4: $y\ \bar{z}\ 1-x$. 5: $\frac{1}{2}-x\ \frac{1}{2}-y\ \frac{1}{2}+z$. 6: $\frac{1}{2}+z\ \frac{1}{2}-x\ \frac{1}{2}+y$. 7: $\frac{1}{2}-z\ \frac{1}{2}-x\ \frac{1}{2}+y$. 8: $1\frac{1}{2}-x\ y-\frac{1}{2}\ 1\frac{1}{2}-z$. 9: $\bar{x}\ \bar{y}\ z$.

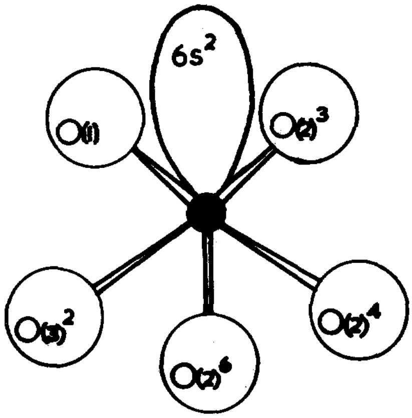

FIG. 2. A schematic depiction of the octahedral environment of each Bi^{3+} ion.

Composition Variability and Metastable Phases

Reference to Table II shows that if the molar ratio of component oxides is varied, the body-centered unit-cell contents $M_{26}O_{40}$ can be maintained by altering the percentage composition of Bi_2O_5. Stoichiometries richer in bismuth require less Bi^{5+} component. The molar ratio 19:1 can be regarded as the equilibrium ratio in the Bi/Zn system because at these concentrations of Bi_2O_3 and ZnO each Bi^{3+} ion is octahedrally coordinated and the smaller Bi^{5+} and Zn^{2+} ions occupy tetrahedral sites in a complete anion lattice. Stoichiometries richer in ZnO result in small Bi^{5+} ions occupying large octahedral holes whilst stoichiometries richer in Bi_2O_3 result in large Bi^{3+} ions occupying small tetrahedral holes. These phases may be regarded as metastable.

Levin and Roth (*3*) commented that the metastable b.c.c. phases are formed by oxide

TABLE VI

BOND ANGLES ASSOCIATED WITH Bi^{3+}–O OCTAHEDRA[a]

Octahedra	Bond angles (°)	
O(1)–Bi(1)^1–O(3)^2	84.2(2.7)	84.5(1.6)
–O(2)^5	81.33(0.77)	80.96(0.50)
–O(2)^3	90.4(2.2)	90.2(1.4)
–O(2)^4	154.6(2.1)	154.2(1.3)
–O(2)^6	60.60(0.42)	60.66(0.27)
–O(2)^7	142.2(2.2)	142.2(1.4)
O(3)^2–Bi(1)^1–O(2)^5	85.1(1.1)	84.63(0.64)
–O(2)^3	173.69(0.94)	173.56(0.47)
–O(2)^4	115.9(2.0)	115.6(1.1)
–O(2)^6	109.2(2.1)	109.4(1.1)
–O(2)^7	65.4(1.1)	65.19(0.61)
O(2)^5–Bi(1)^1–O(2)^3	90.94(0.23)	90.88(0.16)
–O(2)^4	84.97(0.16)	84.97(0.11)
–O(2)^6	136.51(0.83)	136.48(0.57)
–O(2)^7	115.73(0.85)	115.99(0.59)
O(2)^3–Bi(1)^{1a}O(2)^4	68.46(0.60)	68.45(0.42)
–O(2)^6	70.51(0.43)	70.92(0.27)
–O(2)^7	120.89(0.61)	121.09(0.43)
O(2)^4–Bi(1)^1–O(2)^6	120.53(0.55)	120.89(0.40)
–O(2)^7	62.22(0.33)	63.56(0.23)
O(2)^6–Bi(1)^1–O(2)^7	107.46(0.35)	107.13(0.23)
O(3)–Zn–O(3)^9	109.47	109.47

[a] Superscripts refer to the same symmetry transformations as in Table 5 and standard deviations (in parentheses) refer to the least significant digits preceding these.

additions to Bi_2O_3 that involve larger ions such as Cd^{2+}, Ce^{4+}, etc. Presumably these structures involve the large cations occupying tetrahedral sites thereby causing distortions and nonequilibrium condition in the b.c.c. structure.

γ-Bi_2O_3

A new form of Bi_2O_3 was first prepared by Schumb and Rittner (*11*). The bright yellow product analyzed as 99.8% pure Bi_2O_3 and the unit-cell was determined to be b.c.c. with $a = 10.25$ Å. Levin and Roth (*3*) also prepared this γ-Bi_2O_3 and reported that it had the largest cell dimensions of the b.c.c. phases. It is metastable.

It is our belief that γ-Bi_2O_3 has the composition $Bi_{26}O_{40}$, i.e., 99.74% pure Bi_2O_3. The b.c.c. unit-cell contains 40 oxygen atoms, 24 Bi^{3+} ions in octahedral coordination with one Bi^{3+} and one Bi^{5+} ion on each of the two tetrahedral sites.

Chemical analyses of the compounds, particularly for Bi^{5+}, were unsuccessful due to the extreme insolubility of each substance. Microprobe analyses have not been undertaken, but would be of use in confirming the absence of impurities, initially absent from the reaction mixture.

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