

Polymorphism of Bismuth Sesquioxide. I. Pure Bi_2O_3

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Stability relationships of the four polymorphs of bismuth oxide have been determined by means of DTA and high-temperature x-ray studies. The stable low-temperature monoclinic form transforms to the stable cubic form at $730 \pm 5^\circ\text{C}$, which then melts at $825 \pm 5^\circ\text{C}$. By controlled cooling, the metastable tetragonal phase and/or the metastable body-centered cubic (b.c.c.) phase appear at about 645°C . Whereas b.c.c. can be preserved to room temperature, tetragonal will transform to monoclinic between 550 and 500°C . Tetragonal Bi_2O_3 , however, is easily prepared by decomposing bismutite ($\text{Bi}_2\text{O}_3\cdot\text{CO}_2$) at 400°C for several hours. The greatest transition expansion occurs at the monoclinic to cubic inversion, and cubic Bi_2O_3 shows the greatest coefficient of volume expansion. With exposure to air, Bi_2O_3 carbonates and partially transforms to bismutite and an unknown phase.

1. Introduction

Bismuth oxide is assuming an increasing importance in the ceramic field, particularly in the glass and electronics industries. A literature survey of the polymorphism of Bi_2O_3 , in connection with phase studies of the systems $\text{Bi}_2\text{O}_3\text{—B}_2\text{O}_3$ [1]¹ and $\text{Bi}_2\text{O}_3\text{—Nb}_2\text{O}_5$ [2], revealed unexplained inconsistencies in the data and no unequivocal interpretation. Furthermore, it was realized that a conclusive study of the polymorphic relationships would involve an identification of phases at temperature.

A number of investigators [3–10] have reported on temperatures of transitions and phase changes in Bi_2O_3 . Schumb and Rittner [6] have reviewed the work prior to 1943. Table 1 summarizes the literature data through the work of the present authors, and includes, when given, methods of preparation and study, stable and unstable polymorphs, and temperatures of transitions.

It can be seen from the table that both pure and impure forms of Bi_2O_3 have been reported, with disagreement among investigators both as regards the identity and the stability of the pure phases. The essential conclusions which may be drawn from the previously reported data, as given in table 1, are as follows:

(1) All investigators agree that monoclinic (Mon), pseudo-orthorhombic, ($\alpha\text{-Bi}_2\text{O}_3$) is the stable low temperature form.

(2) Schumb and Rittner believe that the tetragonal (Tet), or pseudocubic form ($\beta\text{-Bi}_2\text{O}_3$) is stable above 710°C . Sillén suggested that this form might be simple cubic at higher temperatures. He based his hypothesis, in part, on analogy with cubic (C) As_2O_3 and Sb_2O_3 .

(3) Schumb and Rittner discovered a b.c.c. phase ($\gamma\text{-Bi}_2\text{O}_3$) representing a metastable form of Bi_2O_3 . The finding was confirmed later by Aurivillius and Sillén, who agreed that the unit cell probably contained $\text{Bi}_{26}\text{O}_{39}$.

(4) Gattow and Schröder, from the results of high-temperature x-ray, differential thermal analysis, and linear thermal expansion studies have found only two polymorphs of Bi_2O_3 , namely the low temperature Mon form which transforms reversibly to a high temperature, face-centered cubic form, designated $\delta\text{-Bi}_2\text{O}_3$.

(5) A number of investigators have reported an impure b.c.c. phase, formed by contamination with porcelain, Si, Fe, Al, and other impurities. Sillén suggested the ideal formula type $\text{Me}_2\text{Bi}_{24}\text{O}_{40}$.

(6) Gattow and Schröder² propose the designation δ^* , β^* , γ^* for the impurity forms of C-, Tet-, and b.c.c. Bi_2O_3 , respectively.

(7) Various investigators, usually using a cooling curve method, have reported transition temperatures between 700 and 717°C . Liquidus temperatures vary from 817 to 825°C .

The objective of this work (part I) was to clarify the polymorphic relationships of pure Bi_2O_3 . This could best be accomplished by the method of high-temperature x-ray diffractometry, which avoids the problem of nonquenchable phases. The study was enlarged (part II) to include the effect of oxide additions on the polymorphism of Bi_2O_3 , when a modification of the x-ray furnace permitted the determination of solidus temperatures and even, under favorable conditions, of liquidus temperatures. It was expected that the latter study would provide information on the impure forms.

² Gattow and Schröder [10] report a metastable bismuth oxide phase, Bi_3O_5 , formed under oxidizing conditions and very similar in structure to Tet, $\beta\text{-Bi}_2\text{O}_3$; however, no identifying characteristics other than chemical analysis are given. Moreover, it transforms to $\beta\text{-Bi}_2\text{O}_3$ in about 3 months at 20°C , or more rapidly at $470 \pm 50^\circ\text{C}$, or in a partial vacuum.

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Literature summary on polymorphism of Bi₂O₃

Investigator	Form	Method of preparation	Notes	Method of study	Transition temp.	Melting temp.
Guertler (1903) [3]		From basic nitrate in porcelain crucible.	(Contains 1.3% silic acid)	Cooling curve. Heating curve. Cooling curve.	704±1 °C 705±1 °C	820±2°C 825±5° 860°
Belladen (1922) [4]		Calcination of basic nitrate.		Cooling curve.		817°
Sillén (1937) [5]	α-Bi ₂ O ₃ (Mon) β-Bi ₂ O ₃ (Tet)	Bi(NO ₃) ₃ (aq)+KOH (aq). Condensation of bismuth vapor from graphite furnace, in O ₂ stream.	Stable low-temp. form. May be cubic at higher temperatures. a=10.93 c=5.62 kx.			
	b. c. c.	Fused in porcelain at 900 °C for 5 min or with Al ₂ O ₃ or Fe ₂ O ₃ .	Suggested formula type: Me ₂ Bi ₂₁ O ₄₀ . a=10.08 kx'			
	Cubic Bi ₂ O ₃	Fused in porcelain at 900 °C for 20 min.	Contaminated with silicon, a=5.525 kx.			
Schumb and Rittner (1943) [6]	α-Bi ₂ O ₃ (Mon) β-Bi ₂ O ₃ (Tet)	Purification of C. P. Bi ₂ O ₃ by heating at 750 °C and leaching. Arc between graphite electrode and molten bismuth in O ₂ stream.	99.99±0.06% Bi ₂ O ₃ . Stable below 700 °C. 99.8±0.2% Bi ₂ O ₃ . Stable above 710° a=10.93 c=5.63 kx.	X-ray examination of rapidly cooled Sample	710°	
	γ-Bi ₂ O ₃ (b. c. c.) b. c. c.	Controlled cooling of β-Bi ₂ O ₃ from 750–800 °C in Pt crucible. Fusion (875 °C) of Bi ₂ O ₃ in porcelain and with SiO ₂ .	Metastable; probably Bi ₂₅ O ₃₉ . a=10.245 kx.			
	Cubic Bi ₂ O ₃	Fusion (875 °C) of Bi ₂ O ₃ in porcelain or silica crucible at 875° and water quenching.	Impure phase: a=5.525 kx.			
Aurivillius and Sillén (1945) [7].		Not given.	Stated to be pure Bi ₂ O ₃ .	Cooling curve of a large quantity in Pt crucible.	≈700°	
	γ-Bi ₂ O ₃ (b. c. c.)	Same as Schumb and Rittner (1943).	Probably Bi ₂₅ O ₃₉ . a=10.243 kx.			
Royen and Swars (1957) [8].	β-Bi ₂ O ₃ (Tet)	Quenched molten Bi ₂ O ₃ from "850° or perhaps 920° C".	α-Bi ₂ O ₃ may also be present in minor amt.			
Belayev and Smolaynenov (1962) [9].		Bi ₂ O ₃ calcined at 500 °C/1–1.5 hr.		Visual polythermal.	704°	819°
Gattow and Schröder (1962) [10].	α-Bi ₂ O ₃ (Mon) δ-Bi ₂ O ₃ (Cubic) δ*-Bi ₂ O ₃ β*-Bi ₂ O ₃ γ*-Bi ₂ O ₃	Not given.	100.0±0.1% Bi ₂ O ₃ . Stable low-temp. form. Stable high-temp. form. a=5.66±0.008 Å (at 750 °C). Cubic impurity form. ^a Tetragonal impurity form. ^b Body-centered cubic impurity form. ^c	DTA and high-temp. x ray. High-temp. x ray. X ray. X ray. X ray.	717±7 °C	824±2 °C
Levin and Roth (present work) ^d	Mon Bi ₂ O ₃ Cubic Bi ₂ O ₃ Tet Bi ₂ O ₃ ^e b. c. c. ^f	Commercial "Spec. pure" and ACS Grades. -----do----- -----do----- -----do-----	Stable low-temp. form. Stable high-temp. form, a=5.66 Å (at 750°C). Metastable; formed from super-cooling Cubic Bi ₂ O ₃ . a=10.93 Å c=5.63 Å Metastable; formed from supercooling cubic Bi ₂ O ₃ . Anion impurities may be important. a=10.268 Å.	DTA and high-temp. x ray. High-temp. x ray. DTA and high-temp. x ray. High-temp. x ray.	730±5 °C	825±5 °C

^a Obtained by fast quenching of molten bismuth oxide mixtures heated at 800 to 1000 °C for 15 to 60 min. Bi₂O₃ mixed with: As₂O₃, Sb₂O₃, La₂O₃, Nd₂O₃, Cr₂O₃, SiO₂, SnO₂, TiO₂, V₂O₅, Nb₂O₅, Ta₂O₅, WO₃. The same phase was obtained from aqueous solution in the system Bi₂O₃-MoO₃.

^b Obtained under certain conditions with mixtures of Bi₂O₃ and: Al₂O₃, Ga₂O₃, In₂O₃, Y₂O₃, Tl₂O₃, Fe₂O₃, Cr₂O₃, PbO₂, MnO₂, CeO₂, ZrO₂, ThO₂.

^c Sillén's body-centered cubic (b. c. c.) type. Impurity oxides not listed.

^d See also [1, 2].

^e Pure tetragonal Bi₂O₃ at room temperature can be obtained easily by heating Bi₂O₃·CO₂ (bismutite) at about 400 °C for 2 to 16 hr.

^f A related b. c. c. form is either stable or metastable depending on the cation impurity (discussed in part II).

2. Starting Materials

Two commercially available grades of bismuth oxide were used. One sample was of reported spectrographic purity; the other sample was certified reagent grade (ACS). The results of a qualitative spectrochemical analysis by the Analytical and Inorganic Chemistry Division of the National Bureau of Standards showed that the reagent grade sample contained iron and silicon (0.01 to 0.001%) in significantly higher concentrations than the spectrographic

grade (less than 0.001%). Minor differences between the two samples were observed for a number of other elements (Ag, Al, Ca, Cr, Cu, Mg, Mn, Na, Ni, and Pb), which were each estimated to be present at less than 10 ppm metal in Bi₂O₃.

The following commercially available compounds were used for studying decomposition effects on the polymorphism of Bi₂O₃: bismutite (Bi₂O₃·CO₂), bismuth hydroxide, bismuth nitrate (Bi(NO₃)₃·5H₂O), bismuth subnitrate, bismuth subgallate, and bismuth subsalicylate.

3. Apparatus and Method

Polymorphic relationships in Bi_2O_3 were first deduced from differential thermal analyses of approximately 0.3 g samples. A few experiments on larger samples (approximately 3 g) gave no significant differences. The deduced relationships were then confirmed with the aid of the high-temperature x-ray diffractometer furnace. The diffraction data were obtained with a modification of the diffractometer furnace described by Mauer and Bolz [11]. The essential feature of the modification [12] involved a platinum sample holder to which the powdered samples could be made to adhere by using a thin smear of petroleum jelly. The petroleum jelly volatilizes at a low temperature, leaving the sample adhered to the surface.

It may be noted that the standard quenching technique was of limited value in this study, because the high-temperature form of Bi_2O_3 could not be quenched. However, in experiments dealing with the preservation at room temperature of the Tet and b.c.c. metastable phases a small quench furnace of low heat capacity was used. The furnace enabled one to control the cooling rate between two temperatures prior to quenching.

4. Results and Discussion

4.1. DTA and High-Temperature X-Ray Results

The results of differential thermal analyses of small samples (0.3 g) are summarized in figure 1. Phase identification was verified by comparison with the results obtained from the high-temperature x-ray diffraction experiments, also shown in figure 1.

The basic phase equilibrium relationships are revealed. At $730 \pm 5^\circ\text{C}$, the low temperature Mon form transforms to cubic Bi_2O_3 (C),³ which remains stable up to the melting point, $825 \pm 5^\circ\text{C}$. If the sample is not heated above about 745°C (see high-temperature x-ray results), or is heated very rapidly to higher temperatures, then, on cooling, inversion to the Mon form takes place at 700°C . If some of the Mon form persists above the transition, it will nucleate the inversion, on cooling.

If the C form is heated above about 775°C , considerable supercooling of the C phase occurs, and tetragonal Bi_2O_3 forms at 650 to 645°C . The Tet phase formed in this manner cannot be preserved to room temperature but transforms to the Mon phase at temperatures varying between 550 and 450°C . If, however, the Tet phase is heated, conversion to the cubic form occurs between 660 and 670°C .

Data from the high-temperature x-ray experiments revealed the b.c.c. phase in addition to the Tet phase. The b.c.c. phase appeared at a temperature slightly below that at which the Tet phase formed, and on reheating, the b.c.c. to C transition occurred slightly below that of the Tet to C transition. Once formed the b.c.c. phase could be pre-

³ The x-ray diffraction powder data fit a face-centered cubic cell. Sillén has interpreted the cubic phase as being simple cubic, whereas Gattow and Schröder [10] consider the symmetry to be face-centered cubic.

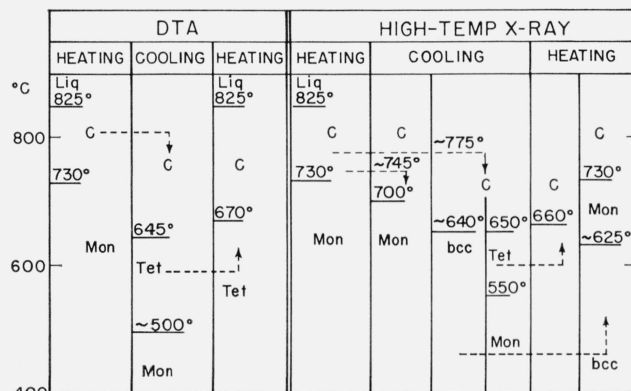


FIGURE 1. Schematic representation of results of differential thermal analysis (DTA) and high-temperature x-ray experiments on Bi_2O_3 .

Dashed arrows indicate changes in direction of the heating and cooling schedule. Polymorphs: Mon—monoclinic, C—cubic, Tet—tetragonal, b.c.c.—body-centered cubic.

served to room temperature by "furnace cooling." Slow heating of the b.c.c. phase from room temperature yielded the stable Mon phase at about 625°C .

A weight-loss determination on 0.3 g of the ACS grade Bi_2O_3 was made simultaneously with a DTA experiment (DTGA) on an independent sample. No detectable change in weight (within 0.001 g) was observed during heating and cooling through the various inversion temperatures.

Figure 2 is a postulated stability diagram for the polymorphs of Bi_2O_3 , based on the data in figure 1 and supported by additional experiments with the low-heat capacity quench furnace, to be discussed later. The ordinate in figure 2 is an undefined measure of stability, for example, free energy of formation or vapor pressure. The metastable melting point of Mon Bi_2O_3 is shown at approximately 800°C , the temperature at which liquid was detected in the high-temperature x-ray furnace during rapid heating of the Mon form.

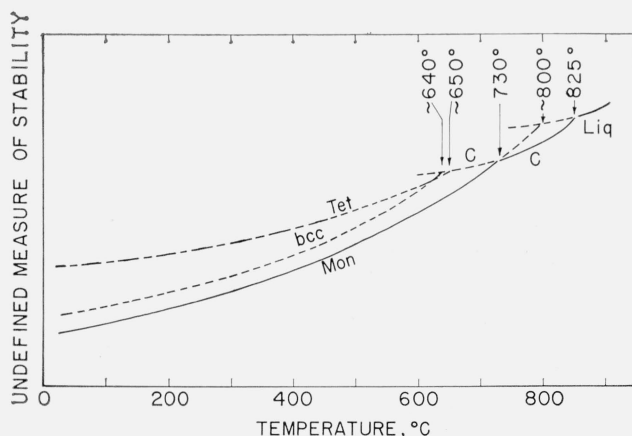


FIGURE 2. Postulated stability diagram of Bi_2O_3 .

Polymorphs: Mon—monoclinic, C—cubic, Tet—tetragonal, b.c.c.—body centered cubic, Liq—liquid.

In the high-temperature x-ray experiments, the Tet phase appeared first on cooling of the C phase and disappeared last when transformation to the C form occurred. Therefore, in figure 2, the metastable C to Tet inversion is shown at a slightly higher temperature than the metastable C to b.c.c. inversion. However, considerable overlapping of the two forms occurred, indicating that the two inversion temperatures are near to each other. Below about 640 °C the b.c.c. phase is shown as more stable than the tetragonal phase, because only the former could be preserved to room temperature by supercooling from high temperatures.

Figure 3 shows a plot of pseudocell dimensions of the various polymorphs of Bi_2O_3 versus temperature. The data were obtained by use of the high-temperature x-ray furnace. For comparison purposes, the cell dimensions were reduced to correspond to a pseudocubic cell volume for two molecules of Bi_2O_3 , according to the arbitrary manner given in the caption of figure 3. The coefficient α of linear thermal expansion for each cell direction was calculated on the original unit cell data by applying least squares to the several sets of data. The cell dimension data were obtained for relatively low 2θ values (below 50°); and, consequently, the accuracy of the thermal expansion values is estimated to be in the order of $\pm 0.2 \times 10^{-5}$.

The pseudo-orthorhombic (Mon) form showed low linear thermal expansion coefficients, namely, 0.5×10^{-5} , 1.3×10^{-5} , and 1.5×10^{-5} Å/Å/deg for the a , b , and c directions, respectively. The average of these three x-ray determined values is 1.1×10^{-5} /deg, in fair agreement with the values reported by Gattow and Schröder [10], using a dilatometric method. Their values ranged from 1.22×10^{-5} /deg at 100 to 200 °C to 1.48×10^{-5} /deg at 575 to 675 °C. The coefficient of linear thermal expansion found in the present work for the C form, 2.4×10^{-5} /deg, is

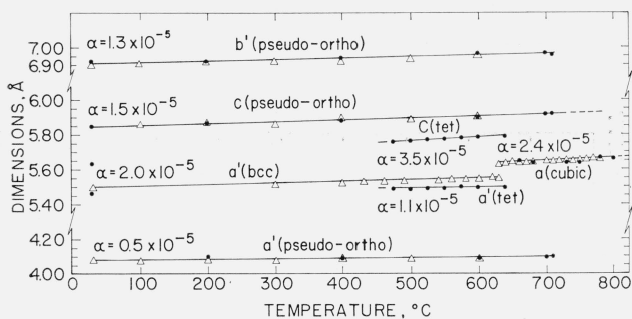


FIGURE 3. Pseudocell dimensions (based on $Z=2$) of the polymorphs of Bi_2O_3 versus temperature.

Cell dimensions have been reduced to correspond to $Z=2\text{Bi}_2\text{O}_3$, in the following arbitrary manner:

- pseudo-orthorhombic—monoclinic polymorph
 $a'(Z=2) = (\frac{1}{2})a(Z=8)$, $b'(Z=2) = (\frac{1}{2})b(Z=8)$, $c(Z=2) = c(Z=8)$.
 - Cubic—cubic polymorph
 $a(Z=2) = a(Z=2)$.
 - Tet—tetragonal polymorph
 $a'(Z=2) = (\frac{1}{2})a(Z=8)$, $c(Z=2) = c(Z=8)$.
 - b.c.c.—body-centered cubic polymorph
 $a'(Z=2) = \sqrt{2/13}$ ($Z=13$).
- α = coefficient of linear thermal expansion, calculated by method of least squares on original data.
- from certified reagent grade (ACS) Bi_2O_3 .
 - △—from "Spec. pure" grade Bi_2O_3 .

almost half that reported by Gattow and Schröder, 4.36×10^{-5} /deg. The c axis for Tet Bi_2O_3 showed the largest coefficient of linear thermal expansion, 3.5×10^{-5} /deg. Based on volume expansion, however, the C form would show the greatest coefficient of expansion (7.2×10^{-5} /deg), and the Mon form, the lowest expansion (3.3×10^{-5} /deg).

Because the different polymorphs of Bi_2O_3 do not have the same number of molecules per unit cell, a comparison of unit cell dimensions is not as instructive as a volume comparison. Figure 4 shows a plot of temperature versus the volumes per molecule of the different polymorphs of Bi_2O_3 . The percentage expansion or contraction at a phase transition is also given.

It may be seen that the Mon phase shows a large expansion, 6.9 percent, when transforming to the C phase at 730 °C. Gattow and Schröder reported a volume expansion at the transition temperature of 4.11 ± 0.06 percent. Thus the present authors obtained a higher percentage of volume expansion at the Mon to C transition temperature and a lower coefficient of linear thermal expansion for the cubic form, than did Gattow and Schröder. Gattow and Schröder used a relatively fast heating rate of $7^\circ/\text{min}$, but the Mon to C transition is not instantaneous

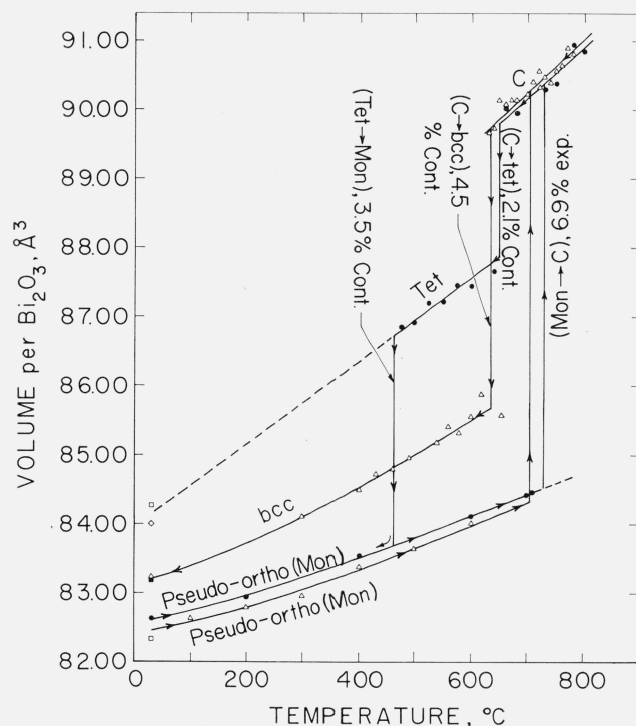


FIGURE 4. Volume per molecule versus temperature for the polymorphs of Bi_2O_3 .

(Calculated from the unit cell dimensions obtained with the high-temperature x-ray diffractometer furnace).

Polymorphs: Pseudo-orthorhombic (Mon)—monoclinic, C—cubic, Tet—tetragonal, b.c.c.—body-centered cubic.

- % exp.—percentage expansion at transition.
- % cont.—percentage contraction at transition.
- from certified reagent grade (ACS) Bi_2O_3 .
- △—from "spec pure" grade Bi_2O_3 .
- ◇—from decomposition of bismutite.
- data taken from Sillén [5].
- data taken from Schumb and Rittner [6].

and occurs over a temperature range. Gattow and Schröder's results may be explained on the basis that in their experiments all of the Mon form did not transform at the inversion temperature but continued to transform during heating of the C phase. Such a situation would lead to an apparently low Mon to C expansion and an apparently high thermal expansion of the C phase.

The C to Tet transition involves a relatively small contraction, 2.1 percent, indicating the similarity in unit cell volumes of the two forms. The contraction in the transition from the C to b.c.c. is 4.5 percent. It is seen that the temperature dependence of the volume per Bi_2O_3 varies for the polymorphs and that the room temperature volume differences are considerably less than at higher temperatures.

4.2. Low-Heat Capacity Furnace Results

The C form of Bi_2O_3 cannot be "quenched" at room temperature. In previous phase equilibrium studies by the present investigators [1, 2] only the Mon phase was obtained in pure Bi_2O_3 by quenching samples in sealed platinum tubes from all temperatures up to 100 °C above the melting point of Bi_2O_3 . The stability diagram (fig. 2), however, indicated a method whereby the metastable phases might be obtained at room temperature, as follows: (a) Heating a sample in a sealed platinum tube to a temperature at which it would be definitely all cubic (above about 775 °C) or liquid. (b) Slow cooling of the sample to about 625 °C, with the possibility that the C phase would be supercooled below 730 °C and would transform to one of the metastable phases. (c) Quenching the metastable phase existing at temperature.

Accordingly, a number of experiments were performed with the low heat capacity furnace in which temperatures and rates of cooling were varied. Identification was by means of the x-ray powder diffraction method applied to the quenched samples.

The essential results are summarized as follows: (a) Pure b.c.c. Bi_2O_3 was formed by heating a sample above the liquidus, at 850 °C for 10 min, cooling to 625 °C in about 45 min, and continued heating at this temperature for 5 min, before quenching.

(b) Body-centered cubic Bi_2O_3 with a trace of Tet Bi_2O_3 could be formed by heating a sample below the liquidus, to 775 °C. The cooling schedule was similar to that in (a).

(c) Pure b.c.c. Bi_2O_3 could be formed readily below the liquidus temperature by a recycling heat treatment, namely, by heating twice to 780 to 785 °C and cooling twice to about 625 °C, before quenching.

(d) These experiments never yielded a large amount of Tet Bi_2O_3 . In several cases, however, the Mon phase was found with a trace of the Tet; it seems probable that at temperature the specimens were Tet.

The work of Royen and Swars [8] is related to the problem of forming Tet Bi_2O_3 from pure bismuth oxide. They formed some Tet Bi_2O_3 by fast quenching of molten Bi_2O_3 from temperatures above about 850 °C. Their work was essentially substantiated in the present investigation, by quenching specimens enclosed in platinum foil envelopes from temperatures of 930 °C (5 min heating period) and 980 °C (1 min heating period). It may be noted that although the Tet phase was present in appreciable amounts, the major phase consisted of Mon Bi_2O_3 . Quenching from the higher temperature did not yield an appreciable higher percentage of the Tet phase. However, samples contained in sealed platinum tubes and quenched from the same temperatures showed only Mon Bi_2O_3 .

4.3. Aging Experiments on Bi_2O_3

During the course of the work, an aging effect on Bi_2O_3 was discovered. Material from a freshly opened bottle of Bi_2O_3 gave an x-ray powder pattern

TABLE 2. Aging experiments on Bi_2O_3

Sample grade	Environment		Time	X ray results ^a
	Atmosphere	Temp.		
		°C	Days	
ACS	Air	≈25	76	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (m)+X ^b (l)
"Spec pure"	Air	≈25	76	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s)+X ^b (l)
ACS	Air	≈25	147	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (tr)+X ^b (l)
"Spec pure"	Air	≈25	147	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s-)+X ^b (l)
ACS	H ₂ O sat. air+C O ₂ ^c	≈25	17	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s+)
"Spec pure"	H ₂ O sat. air+C O ₂ ^c	≈25	17	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (m)
ACS	H ₂ O sat. air+C O ₂ ^c	≈25	55	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s)
"Spec pure"	H ₂ O sat. air+C O ₂ ^c	≈25	55	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (m)
ACS	H ₂ O sat. air	≈25	76	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s-)+X ^b (l)
"Spec pure"	H ₂ O sat. air+C O ₂ ^c	≈25	76	Mon (l)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (m)+X ^b (m)
ACS	H ₂ O sat. air ^d	≈25	167	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (tr)+X ^b (l)
"Spec pure"	H ₂ O sat. air	≈25	167	Mon (m)+ $\text{Bi}_2\text{O}_3\cdot\text{CO}_2$ (s-)+X ^b (m)
ACS	H ₂ O sat. air ^d	140	1	Mon (l)
ACS	C O ₂ ^d	157	1	Mon (l)
ACS	H ₂ O sat. C O ₂ ^d	145	2¾	Mon (l)

^a Mon-monoclinic phase: l—large percentage, m—moderate percentage, s—small percentage, tr—trace.

^b Unknown phase: *d* values of 3.71 Å, 3.68 Å, 3.02 Å (l), 2.74 Å, 2.45 Å.

^c Specimen in stoppered flask, suspended over water, with periodic additions of dry ice.

^d Gas or vapor stream directed through heated chamber containing specimen.

for pure Mon Bi_2O_3 . About six months later, however, material from the same bottle, which had not been desiccated, showed the prominent diffraction peaks corresponding to bismutite ($\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$). The effect of the bismutite formation seemed to be a tendency toward lowering of the temperature of the Mon to C inversion to about 715°C and also toward increasing the probability of forming the b.c.c. phase during supercooling of cubic Bi_2O_3 . This effect may be seen in figure 4, for a sample of spectrographic purity and offers a possible explanation for the lower inversion temperature reported by previous investiga-

tors (see table 1). It should be emphasized, however, that the b.c.c. phase could be formed from pure material, as discussed previously under 4.1 and 4.2, above.

This chance discovery of an aging effect led to a number of experiments (summarized in table 2) in an attempt to accelerate the process. Experiments in which pure Bi_2O_3 was suspended over water in a stoppered flask and to which additions of dry ice were made periodically produced bismutite in small to moderate amounts, after 17 days. At the end of 55 days there was no increase in amount of bis-

TABLE 3. Thermal decomposition experiments on bismuth compounds

Chemical Name	Approximate formula (theoretical ignition loss)	Heat schedule		Total ignition Loss	X ray results ^a
		Temp.	Time		
Bismutite (U.S.P.)	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$ (8.63%)	$^\circ\text{C}$	<i>hr</i>		
		390	1.5	8.08	Tet Bi_2O_3
		390	66	8.65	Tet Bi_2O_3 a -10.9 Å, c -5.62 Å
		490	1.5	8.75	Mon Bi_2O_3
Bismutite (U.S.P.)	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$ (8.63%)	800	1 ^b	8.90	b.c.c. Bi_2O_3 +? (tr)
		200	16	0.29	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$
		300	18	1.05	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$
		350	4	5.47	Tet Bi_2O_3 (l)+ $\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$
		400	18	9.08	Tet Bi_2O_3
		800	$\frac{1}{4}$ ^b		b.c.c. Bi_2O_3
Bismuth subsalicylate (powder, U.S.P.)	$\text{Bi}(\text{C}_7\text{H}_5\text{O}_2)_3 \cdot \text{Bi}_2\text{O}_3$ (35.6%)	775	2		Mon Bi_2O_3
		137	16	0.06	Bismuth subsalicylate (?)
		200	16	.42	Subsalicylate (?) + unknown
		300	16	35.0	Tet Bi_2O_3
		400	16	35.54	Mon Bi_2O_3
		450	16	35.57	Mon Bi_2O_3
Bismuth subgallate (powder)	$\text{Bi}(\text{OH})_2\text{C}_7\text{H}_5\text{O}_7$ (43.4%)	500	16	35.57	Mon Bi_2O_3
		137	16	10.10	Bismuth subgallate (?) ^e
		200	16	14.02	Unknown
		300	16	45.71	Tet Bi_2O_3
		400	16	45.91	Mon Bi_2O_3
		450	16	45.92	Mon Bi_2O_3
Bismuth hydroxide ^d	$\text{Bi}(\text{OH})_3$ (10.4%)	500	16	45.92	
		137	16	0.13	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$ (l)+? (s)
		200	16	.28	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$ (l)+? (s)
		300	16	1.13	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2$
		400	16	8.18	Tet Bi_2O_3 (l)+b.c.c. (s)
		450	16	8.42	b.c.c. Bi_2O_3 (l)+Mon Bi_2O_3 (s)
		500	16	8.46	b.c.c. Bi_2O_3 (l)+Mon Bi_2O_3 (s)
		600	2	8.50	Mon Bi_2O_3 (m)+b.c.c. Bi_2O_3 (m) ^e
700	18	8.50	Mon Bi_2O_3 (l)+b.c.c. Bi_2O_3 (s) ^e		
Bismuth nitrate (crystals, ACS)	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (52.0%)	800 ^f			
		137	16	37.50	Unknown
		200	16	39.58	Unknown
		300	16	45.38	Amorphous (l)+Unknown (m)
		400	16	49.60	Unknown (l)+Tet Bi_2O_3 (m)
		450	16	51.44	Mon Bi_2O_3
		500	16	51.44	Mon Bi_2O_3
Bismuth subnitrate (powder)	$\text{Bi}(\text{OH})_2\text{NO}_3$ (23.6%)	800 ^f			b.c.c. Bi_2O_3 +? (tr) ^f
		137	16	2.95	Amorphous+Unknown
		200	16	4.44	Amorphous+Unknown
		300	16	10.81	Amorphous+Unknown
		400	16	16.52	Intermediate Unknown
		450	16	19.36	Mon Bi_2O_3 +Tet Bi_2O_3 (s)+Intermediate
Bismuth oxyhydroxide ^g	$\text{BiO}(\text{OH})$ (3.72%)	500	16	20.25	Unknown
		135	16	.35	Mon Bi_2O_3
		200	16	.95	Amorphous+Unknown
		250	16	1.57	Amorphous+Unknown
		300	16	1.57	Amorphous+Unknown
		350	17	1.71	Unknown+Mon Bi_2O_3 (s)
		400	7	1.74	Unknown+Mon Bi_2O_3 (m)
		450	7	2.77	Unknown+Mon Bi_2O_3 (m+)
		450	7	5.48	Mon Bi_2O_3
		500	16	5.62	Mon Bi_2O_3
550	16	5.62			

^a Polymorphs: Mon-monoclinic, Tet-tetragonal, b.c.c.-body-centered cubic. Percentages: l-large, m-moderate, s-small, tr-trace.

^b Platinum crucible containing specimen removed from furnace at temperature and immediately chilled by dipping into ice water. (Water did not touch specimen.)

^c Poorly crystalline.

^d Commercially obtained preparation, essentially bismutite by x-ray analysis.

^e d values show shift, indicating smaller unit cell.

^f X ray analysis after a DTA experiment.

^g Prepared in National Bureau of Standards Laboratory by Johan H. deGroot by adding bismuth nitrate to boiling 20 percent NaOH soln., in Pt dish. Material dried at 60°C for 17 hr, then at 85°C for 65 hr.

mutite formed. After 76 days, samples exposed to water vapor and CO₂ or to air at room temperature showed a large amount of an unidentified phase (X in table 2). With continued exposure the unidentified phase, in both experiments, increased at the expense of the bismutite and Mon phases. Attempts to rapidly accelerate the formation of bismutite or the unknown phase by passing over the heated sample a stream of (1) CO₂ gas, (2) CO₂ saturated water vapor, or (3) water saturated air, were unsuccessful (see last 3 experiments of table 2). The aging experiments demonstrate the fact that Bi₂O₃ is reactive under atmospheric conditions and must be tightly sealed and desiccated to avoid compositional changes.

4.4. Thermal Decomposition Experiments

The discovery of bismutite (Bi₂O₃-CO₂) in aged bismuth oxide samples led directly to thermal decomposition studies of bismutite and other bismuth containing organic compounds (see table 3). Approximately 1 g samples were accurately weighed into 30 ml platinum crucibles, heated in an electric resistance furnace at successively higher temperatures, and cooled in air. Ignition losses and x-ray powder diffraction patterns of the samples were obtained for the successive heat treatments.

It is seen from table 3 that bismutite heated at 390 °C for 66 hr or at 400 °C for 18 hr produced pure Tet Bi₂O₃. Within the limit of accuracy of the weight loss measurements, it appears that all of the CO₂ was driven off. At 490 °C, the Tet Bi₂O₃ was transformed to the stable Mon phase. Rapid cooling of a sample from 800 °C, by immersion of the bottom of the crucible in cold water, produced the b.c.c. phase.

Bismuth subsalicylate and bismuth subgallate when heated at 300 °C for 16 hr also yielded pure Tet Bi₂O₃. At the 400 °C heat treatment, the Tet phase was converted to the Mon phase.

The bismuth hydroxide sample, which was shown by x-ray analysis to be mainly bismutite, yielded three forms of Bi₂O₃ during decomposition. A large amount of the tetragonal phase was formed at 400 °C. At 450 and 500 °C, the Tet phase had disappeared, and the sample contained a large amount of the b.c.c. phase plus a small amount of the Mon phase. This transition supports the previously drawn conclusion that, at lower temperatures, the b.c.c. phase is more stable than the Tet phase. The 600 °C heat treatment produced an increasing amount of the Mon phase, at the expense of the b.c.c. phase. The remaining b.c.c. phase showed a shift in diffraction peaks corresponding to smaller *d* values. This shift would be consistent with a decrease in unit cell size, when certain foreign ions are added to pure Bi₂O₃, as will be discussed in part II.

Bismuth nitrate and bismuth subnitrate yielded some Tet Bi₂O₃ during decomposition, but never in major amount. By the end of the 500 °C heat

treatment the samples were all Mon Bi₂O₃. Bismuth oxyhydroxide transformed directly from the amorphous state to the Mon form of Bi₂O₃.

These experiments indicate that the decomposition of organic bismuth compounds at temperatures below 400 °C tend to produce the tetragonal form of Bi₂O₃. If, however, higher temperatures are required for complete decomposition, then the stable Mon Bi₂O₃ phase is formed.

5. Summary

By means of DTA and high-temperature x-ray studies it has been shown that pure bismuth oxide possesses two stable and two metastable polymorphs. A stable reversible transition between the low temperature Mon and the high temperature cubic form occurs at 730 ± 5 °C. The Mon to cubic transition is accompanied by a volume expansion of 6.9 percent. The cubic form shows the greatest coefficient of volume expansion (7.2 × 10⁻⁵/deg). The melting point of the cubic phase is 825 ± 5 °C. Supercooling of the cubic form below the 730 °C Mon transition produces either the metastable tet form at 650 °C or the metastable b.c.c. form at about 640 °C. The results are given in table 1. Whereas by fast cooling, the b.c.c. phase can be preserved to room temperature, the tetragonal phase transforms to the stable Mon phase between 550 and 450 °C. Tetragonal bismuth oxide, however, can be formed readily by the decomposition of bismutite at 400 °C for 18 hr or by the decomposition of bismuth subgallate and bismuth subsalicylate at 300 °C for 16 hr. The Tet bismuth oxide so formed is preserved at room temperature. Bismuth oxide is subject to an aging effect in air and transforms partially to bismutite. With continued exposure an unidentified phase forms.

6. References

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