

Nonstoichiometric Phase with Sillenite-Type Structure in the System $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$

AKITERU WATANABE,* HIROSHI KODAMA,
AND SATOSHI TAKENOUCI

*National Institute for Research in Inorganic Materials, 1-1 Namiki,
Tsukuba-shi, Ibaraki 305, Japan*

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A new compound has been found in the system $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$. It has the composition of 6.73 mol% P_2O_5 and crystallizes in sillenite-type structure with space group $I23$ and $a = 10.1691(1)$ Å. A DTA trace of the compound shows a noticeable endothermic peak around 850°C and an incongruent melting peak at 890°C. Normally the sillenite-type compound has the stoichiometric composition, $\text{Bi}_{24}\text{Me}_2\text{O}_{40}$ ($\text{Me} = \text{Ge}, \text{Si}, \text{or Ti}$); however, the present compound results in the nonstoichiometric one. A structural model is proposed on the assumption that the $24f$ sites are partially occupied by Bi^{3+} ions (occupancy factor 97.22%) and the tetrahedral $2a$ sites are statistically filled by Bi^{5+} and P^{5+} ions. Thus the nonstoichiometric composition within the unit cell is expressed by $\text{Bi(III)}_{23.33}[\text{Bi(V)}_{0.295}\text{P}_{1.705}]\text{O}_{40}$. Using this model, the composition of metastable $\gamma\text{-Bi}_2\text{O}_3$ is discussed. © 1990 Academic Press, Inc.

Introduction

A phase with sillenite-type structure appears in the bismuth-rich portion in systems of bismuth sesquioxide with another oxide or oxides. This phase, in general, has the stoichiometric composition of $\text{Bi}_{12}\text{MeO}_{20}$, where Me represents the second cation (1-4) or a suitable combination of cations (5-8). Furthermore, as shown in Fig. 1, it crystallizes in the body-centered cubic (BCC) system with space group $I23$ (9), where the tetrahedral sites corresponding to the special positions $2a$ are occupied by two Me cations. The lattice constant ranges from 10.10 to 10.27 Å (1-9) depending on the size of Me cation. Two formula weights are contained in the unit cell; consequently the chemical formula, $\text{Bi}_{24}\text{Me}_2\text{O}_{40}$, for this

phase is used hereafter for the sake of convenience.

Nonstoichiometric sillenite-type phases are also reported by several workers (3, 10-14). However, little is known about relationships between the nonstoichiometric composition and the atomic position. For example, in $\text{Bi}_{18}\text{Mg}_8\text{O}_{36} = [\text{Bi}_{18}\text{Mg}_6]\text{Mg}_2\text{O}_{36}$ (12) six small Mg^{2+} ions are statistically located at general positions $24f$ together with 18 large Bi^{3+} ions; at the same time, the oxygen sublattice is deficient by 1/10. This composition seems to be irrational for the sillenite-type structure as discussed in the later section. On one hand, the nonstoichiometric sillenite-type phase found in the system $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ varies in composition depending on the investigators. Levin and Roth (3) estimated the composition to be about 9 mol% P_2O_5 with a very narrow solid-solution region. Batog *et al.* (10) de-

* To whom correspondence should be addressed.

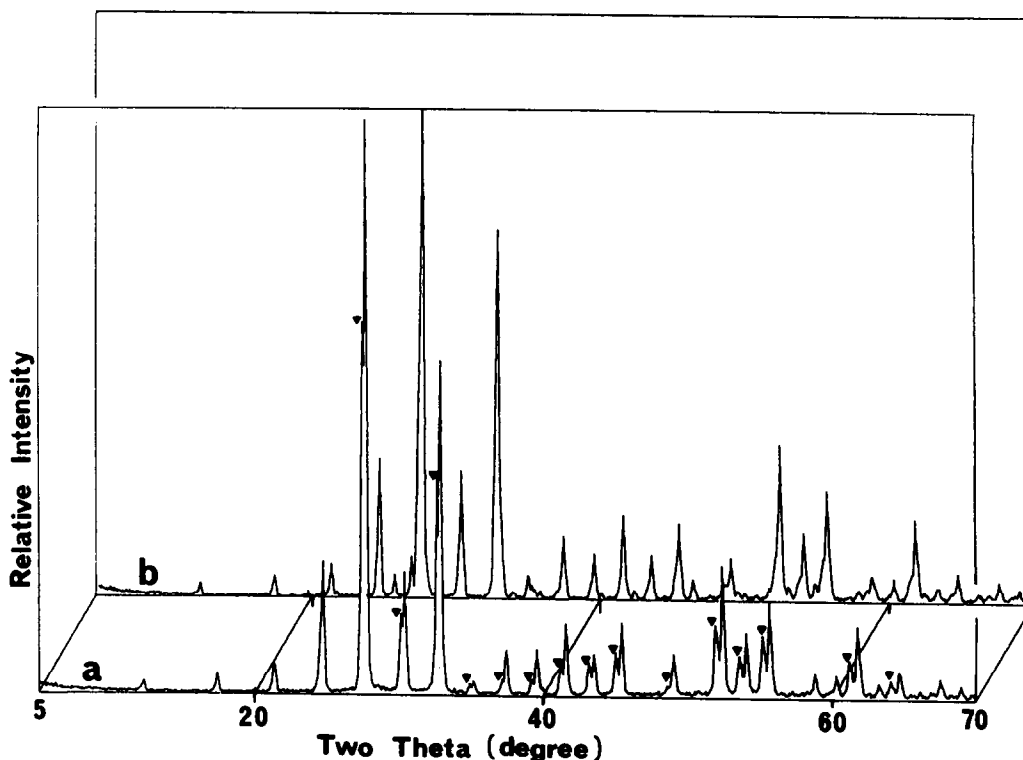


FIG. 2. X-ray diffraction patterns of powder with nominal composition of 4 mol% P_2O_5 . (a) Sample heated at $780^\circ C$ for 40 hr: reflections marked with a solid triangle indicate another phase having BCC symmetry. (b) Sample subsequently annealed at $500^\circ C$ for 200 hr: newly generated reflections for the marked BCC ones are attributed to the low-temperature stable phase, α - Bi_2O_3 , with monoclinic symmetry.

powder diffraction (XRPD) with Ni-filtered $CuK\alpha$ radiation. When the reaction was incomplete after a single heat treatment, the mixture underwent another similar heat treatment. As a result, a line compound with sillenite-type BCC symmetry was found at the nominal composition of 6.5 mol% P_2O_5 . The precise lattice constant $a = 10.1691(1) \text{ \AA}$ was given by the least-squares treatment.

Since the starting material for P_2O_5 was reagent grade $NH_4H_2PO_4$ and since the correct composition of the final product is essential for a close examination into the non-stoichiometry, chemical analyses were conducted using a colorimetric method by the molybdenum blue reaction (15) for the

determination of phosphorous content and using a chelatometric titration with EDTA (xylenol orange indicator and $pH < 1$) (16) for that of bismuth content. The following experimental result for each element is the average of four measurements: 0.939 wt% P (relative mean deviation = 0.186%) and 87.74 wt% Bi (0.006%). These values are converted into the oxide weight percentages: 2.15 wt% P_2O_5 and 97.82 wt% Bi_2O_3 . Therefore we are allowed to consider the composition of this compound to be 6.73 mol% P_2O_5 .

On the other hand, as shown in Fig. 2a, XRPD patterns of the samples with the P_2O_5 poorer composition than 6.73 mol% exhibited two sets of BCC reflections: one

corresponds to the above-mentioned sillenite-type line compound and the other to the new composition having a larger lattice constant than 10.1691 Å. Nevertheless, when these samples were annealed at a lower temperature, e.g., 500°C, the latter new BCC phase transformed to the low-temperature stable $\alpha\text{-Bi}_2\text{O}_3$ phase, which crystallizes in the monoclinic symmetry with the space group $P2_1/c$ (17–19), as indicated in Fig. 2b. On the contrary, since the BCC phase with 6.73 mol% P_2O_5 stood unchanged, this phase is stable at lower temperatures. In other words, the two-phase region exists with composition less than 6.73 mol% P_2O_5 , and a very small amount of P_2O_5 incorporated into the intrinsic Bi_2O_3 brought a metastable BCC phase, which is labeled $\gamma\text{-Bi}_2\text{O}_3$ (17–19), to room temperature as an impurity effect.

The differential thermal analysis (DTA) was carried out as described previously (20). Figure 3 represents a DTA heating curve and a subsequent cooling one for a specimen with 6.73 mol% P_2O_5 . In the heating direction a somewhat complex peak appears first at about 850°C and a second peak at 890°C; the cooling curve does not correspond to the heating one. The disagreement indicates that the specimen melts incongruently at 890°C. In fact, after DTA measurement, the external appearance of the specimen proved that it was in complete molten state at the highest temperature, and an XRPD pattern of it exhibited a mixture of $\alpha\text{-Bi}_2\text{O}_3$ and unknown phase or phases. These results revealed an incongruent melting nature of this sillenite-type phase with 6.73 mol% P_2O_5 . For this reason, we failed to grow the single crystal through slow cooling of the melt with this composition. Devalette *et al.* (13) reported that the sillenite-type phase with 6.25 mol% P_2O_5 transforms reversibly to the high-temperature cubic form at 800°C. In the present DTA curve, however, the thermal effect is observed not around 800°C but at about

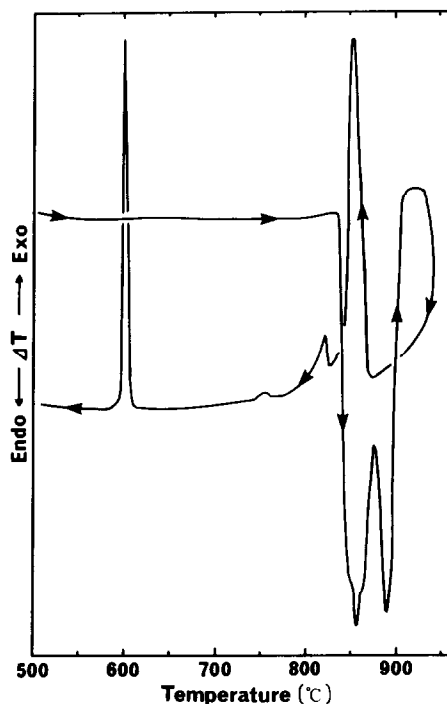


FIG. 3. DTA curve for a sample with composition of 6.73 mol% P_2O_5 measured at a rate of $10^\circ\text{C min}^{-1}$.

850°C. Thus we employed a high-temperature XRPD method to check a structural change for this 850°C endothermic peak. It turned out that the peak corresponds to a gradual transition into a cubic phase. This suggests that the phase equilibria of the present system are not simple. A detailed study of the phase equilibria will be the subject of a future paper.

Discussion

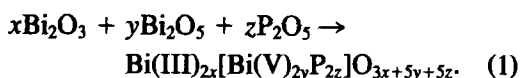
As pointed out by Harwig and Weenk (21) and also as noted from Fig. 1a, the stoichiometric sillenite-type structure contains voids at the $6b$ sites, i.e., $(0, 1/2, 1/2)$, $(1/2, 0, 1/2)$, etc., of the space group $I23$. When, however, we take into account the $6s^2$ lone-pair electrons of Bi^{3+} ion, each void is mostly filled by the four sets of the lone pair of electrons, which point toward the void as

represented by arrows in Fig. 1a. Therefore it appears likely that no ion can interstitially occupy this position. Furthermore, as can be seen from Fig. 1a, this structure does not possess any other interstice.

The full occupation of the tetrahedral sites by *Me* cations seems to be essential to stability of the sillenite-type structure depicted in Fig. 1, because, if any *Me* cation is deficient in the stoichiometric composition, this vacant tetrahedron must be far negatively charged by the four sets of lone pair as well as the four O²⁻ ions forming the tetrahedron. This may result in imbalance of charges over the whole crystal lattice. Thus there seems to be a serious doubt about the partially tetrahedral-site vacant model, Bi(III)₂₄[*Me*(V)_{1.6}□_{0.4}]O₄₀ (i.e., 6.25 mol% *Me*₂O₅, where *Me* = P, As, or V), proposed by Devalette *et al.* (13). In fact, our samples with 6.25 mol% P₂O₅ always yielded a mixture of the sillenite-type phase and the α-Bi₂O₃. Moreover, our preliminary experiments showed that the solid state reaction of Bi₂O₃ with 6.25 mol% V₂O₅ or As₂O₅ afforded no sillenite-type single phase.

Since the sillenite-type phase obtained here contains 6.73 mol% P₂O₅, it can conventionally be expressed by Bi(III)_{93.27}P(V)_{6.73}O_{156.73} = Bi_{27.72}P₂O_{46.58} = Bi₂₄P_{1.73}O_{40.33}. As compared with Bi₂₄*Me*₂O₄₀ for stoichiometric composition, in case all P⁵⁺ ions fully occupy the tetrahedral sites (see the above-stated middle formula), both Bi³⁺ and O²⁻ ions are in considerable excess of those structurally required. On the other hand, if all Bi³⁺ ions are completely located in the general 24*f* positions (see the right-side formula), this model brings about a slight excess of O²⁻ ions and a deficit of P⁵⁺ ions; as mentioned above, the complete occupation of the tetrahedral sites would seem to be the first necessity to the stability of the sillenite-type structure. Accordingly, neither of these models for nonstoichiometry is

adopted. Next, in view of the presence of Bi⁵⁺ ions, we can rewrite the above chemical formula as follows: Bi(III)₂₄[Bi(V)_{0.25}P_{1.75}]O₄₁, where the O²⁻ ions are slightly in excess. Thus, taking these three chemical formulae into consideration, to explain satisfactorily the relationship between the structure and the composition, we assume that no vacancy is formed not only in the tetrahedral sites which are statistically occupied by both Bi⁵⁺ and P⁵⁺ ions but also in the oxygen sublattice. Namely, we start with the following reaction:



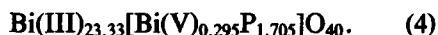
The contents within the unit cell are given by

$$2y + 2z = 2 \quad (2)$$

for the tetrahedral sites, and

$$3x + 5y + 5z = 40 \quad (3)$$

for the oxygen sublattice. From Eqs. (2) and (3) we can uniquely determine a value of *x*, i.e., $x = 35/3 = 11.67$. Therefore, the right side of Eq. (1) is given by Bi(III)_{23.33}[Bi(V)_{2-2z}P_{2z}]O₄₀. Moreover, since $z = (x + y + z) (6.73/100) = (38/3) (6.73/100) = 0.852$ for the phase with 6.73 mol% P₂O₅, the final chemical formula can be written



This means that the Bi³⁺ ions are vacant always only by (2/3)/24 or 2.78% (i.e., two vacant bismuth sites per three unit cells) in the sillenite-type phase of the system Bi₂O₃-Bi₂O₅-*Me*₂O₅. Further, in the present system with *Me* = P, each tetrahedral site is statistically composed of 0.295/2 or 14.75% Bi⁵⁺ and 85.25% P⁵⁺ ions; in this tetrahedral site, the ratio of content of Bi⁵⁺ to that of *Me*⁵⁺ varies with the species of *Me*⁵⁺, because our preliminary experiments showed that the sillenite-type single phase

is not prepared with the composition of 6.73 mol% in the system with $Me = \text{V}^{5+}$ or As^{5+} . At this stage, however, we cannot present structural evidence for this likely model. To determine the actual structure, a single crystal X-ray diffraction analysis or a neutron diffraction analysis is needed.

According to Harwig (19), metastable $\gamma\text{-Bi}_2\text{O}_3$ is isomorphous with or closely related to the sillenite-type $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$ (8). With regard to the composition of $\gamma\text{-Bi}_2\text{O}_3$ within the unit cell, two opinions have been formulated: one is $\text{Bi(III)}_{26}\text{O}_{39}$ (2), where both tetrahedral $2a$ sites are occupied by Bi^{3+} ions and oxygen sublattice is vacant by $1/40$, and the other, $\text{Bi(III)}_{24}[\text{Bi(III)Bi(V)}]\text{O}_{40}$ (4), where one Bi^{3+} ion and one Bi^{5+} ion are statistically located at the tetrahedral sites. The latter model is based on the assumption of the existence of Bi^{5+} ion, though the evidence of it is not obtained by experiments to date. Since it is thought that the Bi^{3+} ion is too large to occupy the tetrahedral hole surrounded by four O^{2-} ions, we can hereupon propose the composition of $\gamma\text{-Bi}_2\text{O}_3$ using the present model expressed by Eq. (4). That is, by substituting the Bi^{5+} ions for all P^{5+} ions in the tetrahedral sites, we can obtain the chemical formula $\text{Bi(III)}_{23.33}\text{Bi(V)}_2\text{O}_{40}$. Probably, even the size of the Bi^{5+} ion seems to be too large for the tetrahedral interstice, so that $\gamma\text{-Bi}_2\text{O}_3$ plays a metastable role in the polymorphs and has a larger unit cell ($a = 10.268 \text{ \AA}$ (3, 17)) than the stable sillenite-type phases (17). On the other hand, the present sillenite-type phase described by Eq. (4) is possible to exist stably, because only 14.75% of the tetrahedral sites tolerably contain the Bi^{5+} ions.

From a stereochemical viewpoint, as shown in Fig. 1, the Bi^{3+} lone-pair character (4, 22) appears to be active in the sillenite-type structure. That is, in this structure a larger ion with lone-pair electrons such as Bi^{3+} , Pb^{2+} , or Sb^{3+} may be situated

in the positions $24f$. Nevertheless, a sillenite-type phase, $\text{Bi}_{24}\text{Pb(II)}_2\text{O}_{38}$, was reported by Levin and Roth ($a = 10.258 \text{ \AA}$) (3) and Kilner *et al.* ($a = 10.2606 \text{ \AA}$) (23). On one hand, since a stoichiometric sillenite-type phase, $\text{Bi}_{24}\text{Pb(IV)}_2\text{O}_{40}$ ($a = 10.262 \text{ \AA}$), was described in a JCPDS card (24), Pb^{2+} ions may be oxidized into Pb^{4+} ions in this structure. At any rate, the Pb^{2+} ions occupy the tetrahedral sites rather than the $24f$ sites. Further, Levin and Roth (3) indicated that the sillenite-type phase does not exist in the system $\text{Bi}_2\text{O}_3\text{-Sb}_2\text{O}_3$, so it may safely be said that the sillenite-type structure appears only in the bismuth-based compounds. Consequently, we are somewhat doubtful of the existence of the sillenite-type compounds, $\text{Bi}_{18}\text{Mg}_8\text{O}_{36}$, $\text{Bi}_{18}\text{Ni}_8\text{O}_{36}$, and $\text{Bi}_{20}\text{Co}_6\text{O}_{39}$, reported by Ramanan *et al.* (12). Actually our preparation of $\text{Bi}_{18}\text{Mg}_8\text{O}_{36}$ gave not a sillenite-type phase but a mixture described by Levin and Roth (3). In addition, no intermediate compound exists in the system $\text{Bi}_2\text{O}_3\text{-NiO}$ (3).

In conclusion, the sillenite-type phase found in the system $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ may be expressed by Eq. (4). That is, the $24f$ sites in the space group $I23$ are partially occupied by Bi^{3+} ions with each site having an average occupancy of 23.33/24 or 97.22%, and no vacancy in the other available sites. Probably, this structural model may apply well in the cation-deficient nonstoichiometric sillenite-type phase.

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