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Polymorphism in Bi_2WO_6

AKITERU WATANABE

National Institute for Research in Inorganic Materials, 1-1 Namiki,
Sakura-mura, Niihari-gun, Ibaraki 305, Japan

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The polymorphism of Bi_2WO_6 has been studied using differential dilatometry and differential thermal analysis with polycrystalline specimens prepared by sintering the oxides Bi_2O_3 and WO_3. Two reversible polymorphic transitions were observed, one at 662°C and one at 962°C. The former transition showed a very small change of enthalpy and very little dimensional change, while the latter showed a large thermal hysteresis, had a large change of enthalpy, and was accompanied by a sizable volume change. The high-temperature powder X-ray data indicated that the intermediate phase as well as the low-temperature form had orthorhombic symmetry and the high-temperature form had monoclinic symmetry. The 662°C transition is displacive and the 962°C transition reconstructive. A crystal structure of the high-temperature form is proposed and discussed in comparison with that of the low-temperature form.

Introduction

Bismuth tungstate, Bi_2WO_6, is the simplest member of the bismuth oxide layer structure family (*1, 2*), and the room-temperature crystal structure consists of a regular stacking of Bi_2O_2 layers interleaved with WO_4 layers containing corner-linked WO_6 octahedra (*3*). This compound is regarded as ferroelectric with high transition temperature of 920–960°C (*4–8*) and large spontaneous polarization (*3*). This reversible phase transition showed a large thermal hysteresis (*9, 10*) and underwent a remarkably discontinuous volume change (*11*), so that grown large single crystals inevitably cracked at about 860°C (*5, 9, 10*) on cooling to room temperature. On the other hand, no success was obtained in attempts to determine the structure of the high-temperature modification of Bi_2WO_6; namely, according to Newkirk *et al.* (*5*), the high-temperature powder X-ray diffraction measurements ended in failure because of the severe recrystallization above 850°C, and moreover the quenching of the high-temperature phase from 1030°C to room temperature was never achieved because of the inevitable reversibility of the transition.

In the present paper, the polymorphic transformations of Bi_2WO_6 were studied by differential dilatometry and differential thermal analysis (DTA), and the structure of the high-temperature form was inferred from the results of high-temperature X-ray diffraction.

Experimental

Polycrystalline sample preparation was the same as previously described (*10*). The sample was checked by X-ray powder diffraction method using Ni-filtered Cu$K\alpha$ radiation. Results agreed well with those of

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orthorhombic Bi_2WO_6 reported by Wolfe *et al.* ($a = 5.457, b = 5.436$, and $c = 16.427$ Å; space group $B2cb$ and $Z = 4$) (*3*).

The ways in which the DTA and dilatometric measurements were performed were described elsewhere (*12*). A bar of Bi_2WO_6 for dilatometry was prepared in the same way as reported previously (*13*).

The high-temperature X-ray diffractometry was indispensable for structure determination of the nonquenchable high-temperature form. The powder diffraction data were obtained with a high-temperature X-ray diffractometer furnace such as described by Levin and Mauer (*14*); at the same time, the measurements were accomplished by diluting the sample with platinum powder (under 200 mesh). This dilution solved both problems of severe recrystallization above 850°C and abrupt volume expansion at the transition temperature of about 940°C. Moreover, diffraction lines from platinum powder were used as an internal standard. The temperature accuracy was ±5°C. The cell dimensions were refined with a least-squares treatment.

Results and Discussion

Figure 1 shows the typical dilatometric curves for heating and cooling cycles. The lower curve corresponds to the first cycle and the upper one to the final fifth cycle. In the first heating curve, a very small inflection is observed at 650°C; on further heating, the bar sample contracts owing to sintering in the temperature range 780 to 935°C, and at 935°C a sudden large expansion occurs. This thermal expansion behavior of Bi_2WO_6 resembled that of γ-Bi_2MoO_6 (*12*) because of their structural similarity (*3, 15*). On cooling, a contraction corresponding to the expansion at 935°C occurs suddenly at 860°C to show a large thermal hysteresis. The temperature of 860°C agreed precisely with the destructive phase transition temperature observed from the single crystal growth experiments (*5, 9, 10*). However, the change in length of the sample differs sharply in the heating and cooling cycles, in good agreement with the dilatometric results by Streicher (*11*). Therefore, the bar becomes longer and longer during cyclic heat treatment as shown in Fig. 1. This apparent expansion of the bar is due to gaps produced by cracks which were generated by the strain developed on cooling through the transition temperature of 860°C. In fact, many noticeable cracks were observed on the bar after the measurements. In the final heat treatment, the cooling curve shows two inflections, a large one at 860°C and a very small one at 650°C. The latter small inflection has already been observed on the first heating curve at the same temperature.

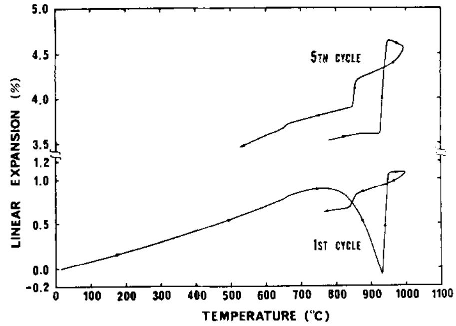

FIG. 1. Thermal expansion behavior of Bi_2WO_6 in a series of heating and cooling cycles in the temperature range 780 to 990°C at a rate of 5°C min^{-1}.

Below the melting point, DTA thermograms also indicated two endothermic peaks on heating, a quite small one at 662°C and a large one at 962°C; however, on cooling to room temperature, a single distinct exothermic peak was observed at 856°C but no thermal effect was detected below that temperature, because the heat of the former transition at 662°C was very small and the corresponding exothermic peak was therefore diffuse in the cooling.

The dimensional changes in thermal expansion may be premonitory indications of the true transition (*16*), so that the transition temperatures determined by DTA rather than by dilatometry were adopted as the polymorphic transition ones. Thus, from these thermoanalytical results, it is concluded that Bi_2WO_6 undergoes two reversible polymorphic transitions, one at 662°C and one at 962°C. In other words, the low-temperature stable form (for brevity indexed *l*) exists below 662°C, the intermediate phase (for brevity indexed *i*) in the range 662 to 962°C, and the high-temperature stable form (for brevity indexed *h*) above 962°C. The 962°C transition showed a large thermal hysteresis, had a large enthalpy change (1 kcal $mole^{-1}$ (*5*)), and was accompanied by a sizable volume change; in particular, this volume change gives rise to disruptive cracks in grown single crystals on cooling. Accordingly, this transition was easily observed by several investigators, whereas the transition at 662°C has not been found so far owing to the very small enthalpy change and to very little dimensional change.

Winger *et al.* (*17*) reported that Bi_2WO_6 may have three polymorphic transitions, one at 885°C, one at 935°C, and one at 965°C. Likewise, Wolfe *et al.* (*3*) stated that, in addition to a 940°C transition, Bi_2WO_6 underwent two polymorphic transitions above 940°C; however, these two temperatures were not given. The discrepancy between these workers' results and the present ones may be attributed to the composition of the sample. If the sample contains small amounts of a second phase of a neighboring intermediate compound in the Bi-rich portion, the DTA results would show more than one phase transition above 800°C; in fact, a sample which had $Bi_2O_3:WO_3$ molar ratio of 21:19 (52.5 mole% Bi_2O_3) gave DTA results similar to those by Winger *et al.* (*17*). Therefore, it appears that the samples prepared by these workers were not uniform.

According to Hoda and Chang (*18*), $Bi_2W_2O_9$ was thermostable between 675 and 925°C; below 675°C, this phase was considered to be decomposed into Bi_2WO_6 and WO_3, because a solid-state reaction of Bi_2O_3 and WO_3 in the ratio 1 : 2 yielded only a mixture of Bi_2WO_6 and WO_3 rather than the compound $Bi_2W_2O_9$ at temperatures below 675°C, despite heat treatment for 4 weeks. Hence, if the sample of Bi_2WO_6 contains small amounts of WO_3, the thermal effect at 662°C observed here may be related to the $Bi_2W_2O_9$ decomposition reaction. However, the thermal stability experiments performed by Watanabe and Goto (*19*) indicated that $Bi_2W_2O_9$ was thermostable at temperatures below 675°C in comparison with Bi_2WO_6 and WO_3. Furthermore, below the melting point, no thermal effects were detected in $Bi_2W_2O_9$ by both DTA and dilatometry. Therefore, the thermal effect at 662°C is attributed to the polymorphic transition of Bi_2WO_6.

High-temperature X-ray data indicated no detectable change around 650°C in contrast to the dilatometric results. That is, the lattice parameters (*a*, *b*, and *c*) elongated consistently with increasing temperature below 940°C as described by Ismailzade and Mirishli (*4*) and Newkirk *et al.* (*5*); however, a powder pattern taken above 940°C was quite different from that of $Bi_2WO_6(i)$. This suggests that $Bi_2WO_6(i)$ probably possesses orthorhombic symmetry, and that the $Bi_2Wo_6(l) \rightarrow Bi_2WO_6(i)$ transition is displacive and the $Bi_2WO_6(i) \rightarrow Bi_2WO_6(h)$ transition is reconstructive.

According to Cross (*2*), optical observations of single crystals indicated that the symmetry of Bi_2WO_6 above 950°C was lower than tetragonal. In addition, it was seen from the present study that the powder pattern of $Bi_2WO_6(h)$ resembled a room-temperature X-ray pattern of $BiLaWO_6$ (*20, 21*) which was monoclinic ($P2/c$) with a = 8.313, b = 7.716, c = 16.482 Å, and β = 102.23°. The pattern of $Bi_2WO_6(h)$ was therefore explained using

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR Bi_2WO_6 AT 985°C AND $BiLaWO_6$ AT ROOM TEMPERATURE

	Bi_2WO_6[a]			$BiLaWO_6$[b]		
h k l	d_{calc} (Å)	d_{obs} (Å)	I_{obs}	d_{calc} (Å)	d_{obs} (Å)	I_{obs}
1 0 0	8.169			8.124	8.186	2
0 0 2	8.019	7.922	3	8.054	8.117	4
−1 0 2	6.462			6.443	6.438	8
1 0 2	5.190			5.196	5.200	2
2 0 0	4.085	4.011	7	4.062	4.028	6
0 0 4	4.010			4.027		
−2 0 2	4.006			3.982	3.956	4
0 2 1	3.749			3.752	3.755	2
−1 2 1	3.474			3.472	3.473	3
2 0 2	3.358	3.364	30	3.353	3.351	70
1 2 1	3.344			3.344		
−2 0 4	3.231	3.231	10	3.211	3.219	60
0 2 3	3.127	3.125	5	3.133	3.133	100
−1 2 3	3.052			3.472	3.473	3
−2 2 1	2.834	2.837	4	2.827	2.825	68
−3 0 2	2.767			2.749	2.746	3
3 0 0	2.723	2.722	4	2.708	2.705	5
2 2 1	2.695	2.673	100	2.691	2.685	32
0 0 6	2.673			2.685		
2 0 4	2.595			2.598	2.600	1
−3 0 4	2.519	2.521	1	2.507	2.503	3
−2 0 6	2.497			2.496		
−1 2 5	2.477			2.481	2.474	3
0 2 5	2.466			2.473		
−3 2 3	2.195	2.195	2	2.187	2.186	4
−3 0 6	2.154	2.153	2	2.148	2.146	4
3 2 1	2.152			2.146		
−4 0 2	2.090	2.091	2	2.076	2.075	12
3 0 4	2.056			2.055	2.053	2
−1 0 8	2.052			2.059		
2 0 6	2.044			2.049		
4 0 0	2.042			2.031	2.030	3
0 0 8	2.005	2.005	1	2.013	2.008	1
−4 0 4	2.003			1.991	1.993	4
−3 2 5	2.000			1.995		
0 2 7	1.970	2.002	2	1.976	1.975	20
2 2 5	1.971			1.974		
3 2 3	1.936	1.928	1	1.934	1.929	24
0 4 0	1.928			1.929		
−2 2 7	1.919	1.922	1	1.920	1.922	20

[a] Lattice constants: $a = 8.366$, $b = 7.711$, $c = 16.426$ Å, and $\beta = 102.46°$.

[b] d°: $a = 8.313$, $b = 7.716$, $c = 16.482$ Å, and $\beta = 102.23°$.

the lattice parameters of $BiLaWO_6$. The precise lattice parameters determined by the least-squares method were $a = 8.358$, $b = 7.707$, $c = 16.420$ Å, and $\beta = 102.46°$ at 969°C; and $a = 8.366$, $b = 7.711$, $c = 16.426$ Å, and $\beta = 102.46°$ at 985°C. Table I gives the observed and calculated *d*-values for $Bi_2WO_6(h)$ at 985°C along with those of $BiLaWO_6$ for comparison. The diffracted intensity distribution of $Bi_2WO_6(h)$ was different from that of $BiLaWO_6$ because of preferred orientation of $(00l)$ planes, and because peaks with weak intensity could not be observed owing to the low signal-to-background ratio in high temperature diffractometry.

The high-temperature structures are generally of higher symmetry than the low-temperature structures in thermal phase transitions. In Bi_2WO_6, however, the symmetrical relation was reversed; namely, $Bi_2WO_6(h)$ has monoclinic structure, while $Bi_2WO_6(l)$ and $Bi_2WO_6(i)$ both have orthorhombic structures. Likewise, the orthorhombic low-temperature γ-form of Bi_2MoO_6 (*15*) with $Bi_2WO_6(l)$-related structure was also transformed to the monoclinic high-temperature γ'-form (*22*) through the metastable γ''-phase (*12*) which had orthorhombic symmetry (*23*). Thus, in view of their structural similarity, it is natural that $Bi_2WO_6(l)$ undergoes the same symmetrical changes as those of γ-Bi_2MoO_6 by polymorphic transformations.

The structure of $Bi_2WO_6(h)$ can be derived from that of $BiLaWO_6$, inasmuch as these two compounds would appear to be isomorphous. The compound $BiLaWO_6$ formed a solid-solution series $Bi_{2-x}La_xWO_6$ with $x = 0.4$–1.1 (*20, 21*). Recently, Watanabe *et al.* (*24*) have determined the crystal structure of $Bi_{1.4}La_{0.6}WO_6$ from an ultrahigh resolution lattice image obtained in a high voltage electron microscope: the structure consisted of $Bi_{1.4}La_{0.6}O_2$ layers interleaved with WO_4 layers containing WO_4 tetrahedra with no oxygens in common. Hence the structure of $Bi_2WO_6(h)$ may consist of Bi_2O_2 layers sandwiched between the same WO_4 layers as mentioned above. In short, $Bi_2WO_6(l)$ and $Bi_2WO_6(i)$ both have W in 6-coordination; $Bi_2WO_6(h)$ is quite different with 4-coordinated W. Since all modifications for Bi_2WO_6 have layered structures, the polymorphic transitions are completely reversible. In Bi_2MoO_6, on the contrary, the γ'-form had no layer-type structure (*22*) and moreover the γ''-form was metastable phase (*12*), so that the $\gamma'' \rightarrow \gamma'$ transition was irreversible (*12*). Figure 2 shows the proposed crystal structure of $Bi_2WO_6(h)$ together with those of $Bi_2WO_6(l)$ (*3*) and La_2MoO_6 (*25*) for comparison. As is obvious from Figs. 2A and B, in Bi_2WO_6, the main orientation relations are found to be $[110]_l//[100]_h$ and $[\bar{1}10]_l//[010]_h$. The unit cell of $Bi_2WO_6(h)$ is related to that of $Bi_2WO_6(l)$ as follows: $a_h \simeq b_h \simeq \sqrt{2}(a_l + b_l)/2; c_h \simeq c_l$. The difference in the tungsten coordination appears to depend on the degree of the $6s^2$ lone-pair character of Bi^{3+}. That is, in both $Bi_2WO_6(l)$ and $Bi_2WO_6(i)$ the lone-pair character is dominant, so that each Bi^{3+} forms the fifth pair bond with an oxygen of the WO_4 layer (*3, 26*); as a result, the WO_4 layer consists of corner-linked WO_6 octahedra. On the other hand, in $Bi_2WO_6(h)$ the lone-pair character is constrained by thermal energies; therefore, the bond does not exist between the Bi_2O_2 layer and the WO_4 layer, in which the isolated WO_4 tetrahedra are eventually formed. Similarly, the com-

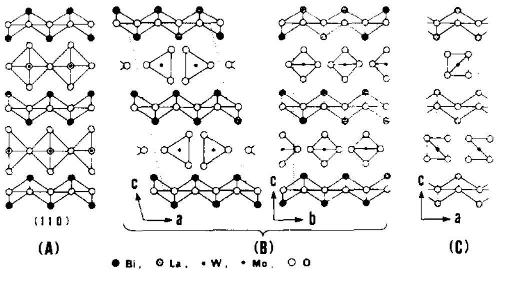

FIG. 2. Schematic representation of the crystal structures: (A) the idealized structure of Bi_2WO_6 at room temperature projected on (110); (B) a proposed crystal structure of the high-temperature stable form of Bi_2WO_6 projected on (010) and (100); and (C) the structure of La_2MoO_6 projected on (100).

pound La_2MoO_6 has a layered structure which consists of alternating La_2O_2 layers and MoO_4 layers as illustrated in Fig. 2C. However, the La^{3+} ion does not form the fifth pair bond with an oxygen of the MoO_4 layer because of the spherical outer electron configuration ($5s^25p^6$), so that the La_2MoO_6 has tetragonal symmetry with $a = 4.088$ and $c = 15.99$ Å (*25*), and has the MoO_4 layers containing isolated MoO_4 tetrahedra.

According to Newkirk *et al.* (*5*), the $Bi_2WO_6(h)$ boules produced by the Czochralski method cracked on cooling to yield small prismatic $Bi_2WO_6(l)$ rods surrounded with $((001))_l$ and $((111))_l$ faces; namely, the angle between these two cleavage faces was found to be 102.8° from observation and to be 103.8° from calculation. In addition we notice that this angle is nearly equal to the lattice parameter β of $Bi_2WO_6(h)$. Therefore, the Czochralski pulling direction is found to be $[\bar{1}10]_l$ or $[010]_h$, i.e., the b axis of $Bi_2WO_6(h)$. This suggests that the single crystal of $Bi_2WO_6(h)$ splits at 860°C on cooling through the destructive transition along the planes parallel to $(100)_h$ and $(001)_h$ planes represented by dotted lines projected on the $(010)_h$ plane in Fig. 2B; as a result, the foregoing prismatic rods were formed. These cleavage planes reasonably break through the weak-bonded portions of the structure of $Bi_2WO_6(h)$. Thus, the experimental results observed by Newkirk *et al.* were fully explained from the $Bi_2WO_6(h)$ structure proposed here.

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