Preparation and Crystal Structure of the Titanium and Hafnium Bismuthides Ti₈Bi₉ and Hf₈Bi₉

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The titanium bismuthide Ti_8Bi_9 has been prepared by reaction of the elemental components in evacuated, sealed silica tubes and also by arc-melting. Its crystal structure is of a new type, which was determined from single-crystal X-ray data: $P4/nmm$, $a = 1027.7(1)$ pm, $c = 737.5(1)$ pm, $Z = 2$, $R = 0.027$ for 553 structure factors and 32 variable parameters. The titanium atoms occupy four different sites: two with octahedral and two with square-antiprismatic bismuth coordination. The bismuth atoms are located at three different sites with four, five, and seven titanium neighbors. An analysis of the Ti–Bi bonding distances (covering the range between 282 and 314 pm) leads to the conclusion that there are Ti–Ti bonding interactions (at distances between 293 and 307 pm). In addition, some weakly bonding Bi–Bi interactions (334–353 pm) are assumed. The compound Hf_8Bi_9 has the same structure: $a = 1071.8(1)$ pm, $c = 752.0(1)$ pm.   © 1997 Academic Press

INTRODUCTION

The binary system titanium–bismuth has only been investigated on the titanium-rich side. Obinata, Takeuchi, and Saikawa identified two compounds in this system, which they characterized through X-ray powder patterns (1). A compound close to the composition Ti_3Bi is in equilibrium with the hexagonal modification of titanium. This is probably the same phase as the one reported earlier with the tentative composition "Ti_4Bi" (2, 3). Obinata *et al.* observed a phase γ in samples with a higher content of bismuth, to which they assigned a composition close to Ti_2Bi. The powder pattern of this compound, however, seems to be different from the one reported by Auer-Welsbach, Nowotny, and Kohl (3) for a compound with this composition. The atomic positions of the latter compound have been determined (3). They belong to the space group $I4/mmm$, which was also found for the seemingly isotypic compound La_2Sb (4).

We have recently redetermined the crystal structure of "Ti_2Bi" in two independent single-crystal investigations, where we confirm the space group $I4/mmm$ (5, 6). However, in both investigations an additional atomic site has been found to be occupied by a light atom. Since it is coordinated octahedrally by six titanium atoms (at distances between 203 and 228 pm) it is well suited for oxygen, which may have been introduced as an impurity. The compositions of this phase resulting from the structure determinations are $Ti_{3.0(1)}Bi_2O$ (5, 6) and $Ti_{3.10(4)}Bi_2O$ (6), and the structure of this compound is very similar to that reported for Eu_4As_2O (7).

Samples with higher content of bismuth have also been characterized in our laboratory. A compound with the approximate composition $\sim TiBi$ has been described by Block (8). Its Guinier powder pattern has at that time been indexed with a tetragonal cell (8, 9), which is confirmed now. The presently reported structure determination of this compound resulted in the composition Ti_8Bi_9. Since we have shown that "Ti_2Bi" is in fact a ternary compound (5, 6), Ti_8Bi_9 is the first structurally characterized binary titanium bismuthide. Preliminary results of this work have been presented at a conference (10).

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

The compounds were prepared from powders of the elements, all with nominal purities $\geq 99.9\%$. Cold-pressed pellets of the ideal composition were annealed in evacuated, sealed silica tubes at 400°C for one day, followed by two weeks at 800°C, and furnace cooling.

The samples react with the humidity of the air and must therefore be kept under argon or dry paraffin oil. Compounds with high titanium content have been reported to be pyrophoric (3); however, samples with a higher content of bismuth may not react that readily with air. This has not been investigated any further. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope

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were in good agreement with the ideal composition and did not reveal any impurity elements heavier than sodium.

Guinier powder diagrams of the samples were recorded with $CuK\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. For this purpose the samples were ground to a fine powder under dry paraffin oil. During the exposure to X-rays the powders were placed together with the paraffin oil between two thin polymer foils. Indices could be assigned on the basis of the earlier reported tetragonal cell (9). The identification of the diffraction lines was facilitated by intensity calculations (11) using the positional parameters obtained from the single-crystal investigation. The lattice constants were refined by least squares fits. Ti_8Bi_9 has a noticeable homogeneity range. For a furnace cooled sample with a starting ratio $Ti : Bi = 1 : 1$ the lattice constants $a = 1027.7(1)$ pm, $c = 737.5(1)$ pm, $V = 0.7789(1)$ nm^3 were obtained. For a sample of the overall composition $1 : 2$, annealed for one week at $500°C$, the lattice constants are greater: $a = 1028.4(1)$ pm, $c = 738.3(1)$ pm, $V = 0.7808(1)$ nm^3. For the isotypic compound Hf_8Bi_9 the lattice constants are $a = 1071.8(1)$ pm, $c = 752.0(1)$ pm, $V = 0.8639(1)$ nm^3.

STRUCTURE DETERMINATION

A single crystal of Ti_8Bi_9, isolated from a sample with the overall composition $1 : 1$, was used for the structure determination. It was sealed into a thin-walled silica tube to prevent its reaction with air. Intensity data were recorded on an Enraf-Nonius four-circle diffractometer using graphite-monochromated $MoK\alpha$ radiation and a scintillation counter with pulse-height discrimination. The background was determined at both ends of each $\theta/2\theta$ scan. An empirical absorption correction was applied from psi scans. Because of the high absorption of the heavy bismuth atoms a further absorption correction was made assuming a spherical crystal shape. The lattice constants determined on the four-circle diffractometer ($a = 1026.6(1)$ pm, $c = 737.6(1)$ pm) are in good agreement with those obtained from the powder data (Table 1).

The structure was determined with the aid of the SHELXL-93 program system (12) using direct methods. It was refined in the space group $P4/nmm$, the space group of the highest symmetry compatible with the observed systematic extinctions. A full-matrix least-squares program (13) was used with atomic scattering factors (14) corrected for anomalous dispersion (15). The weighting scheme included a term which accounted for the counting statistics, and a factor correcting for secondary extinction was optimized as a least-squares parameter. All atoms were refined with anisotropic displacement parameters. To check for deviations from the ideal composition, the occupancy factors were allowed to vary, together with the thermal parameters, during one series of least-squares cycles during which the

scale factor was held constant. No serious deviations from the ideal occupancies were observed (Table 2), and in the last least-squares cycles the ideal values were resumed. The positional parameters were standardized using the program STRUCTURE TIDY (16). The interatomic distances are given in Table 3. Listings of the structure factors and the anisotropic thermal parameters are available from the authors (17).

DISCUSSION

Ti_8Bi_9 crystallizes with a new structure type (Fig. 1), which we have also found for Hf_8Bi_9. Attempts to prepare the isotypic zirconium compound have so far not been successful, possibly because zirconium has a larger size than

TABLE 1
Crystal Data for Ti_8Bi_9[a]

Structure type	Ti_8Bi_9
Space group	$P4/nmm$ (Nr. 129)
Lattice constants from Guinier powder data	
a (pm)	1027.7(1)
c (pm)	737.5(1)
V (nm^3)	0.7789
Formula units/cell	$Z = 2$
Formula mass	2264.0
Calculated density (g/cm^3)	9.65
Crystal dimensions (μm^3)	$40 \times 40 \times 20$
$\theta/2\theta$ scans up to	$2\theta = 73°$
Range in h, k, l	$\pm 16, \pm 16, 0 \leq l \leq 11$
Total number of reflections	7514
Highest/lowest transmission	1.93
Unique reflections	1092
Inner residual	$R_i = 0.057$
Reflections with $I > 3\sigma(I)$	553
Number of variables	32
Extreme residual electron densities (e/Å^3)	$+3.1/-5.5$
Conventional residual	$R = 0.027$
Weighted residual	$R_w = 0.038$

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

TABLE 2
Atomic Parameters of Ti_8Bi_9[a]

Atom	$P4/nmm$	Occupancy	x	y	z	B
Ti1	8i	1.02(1)	1/4	0.6072(4)	0.1538(5)	0.68(7)
Ti2	4d	1.00(1)	0	0	0	0.61(5)
Ti3	2c	1.01(3)	1/4	1/4	0.0766(13)	1.4(1)
Ti4	2c	0.91(3)	1/4	1/4	0.5781(11)	0.81(9)
Bi1	8j	1.001(2)	0.08512(6)	0.08512(6)	0.3478(1)	0.644(7)
Bi2	8i	0.998(2)	1/4	0.01165(9)	0.8094(1)	0.59(1)
Bi3	2b	0.990(5)	3/4	1/4	1/2	0.95(2)

[a] The occupancy parameters were obtained in a separate series of refinement cycles. In the final cycles the ideal occupancy parameters were used. The last column contains the equivalent isotropic B values (in units of 10^4 pm^2).

TABLE 3
Interatomic Distances in the Structure of Ti$_8$Bi$_9$^{a}

Ti1:	1Bi2	281.8(4)	Ti4:	4Bi1	293.7(5)	Bi2:	1Ti1	281.8(4)
	1Bi3	294.5(4)		4Bi2	298.5(5)		2Ti2	293.1(1)
	2Bi1	297.1(4)		1Ti3	368(1)		1Ti4	298.5(5)
	2Bi2	307.5(2)		1Ti3	370(1)		2Ti1	307.5(2)
	1Ti1	293.4(6)	Bi1:	1Ti2	284.8(1)		1Ti3	314.4(6)
	2Ti2	301.7(2)		1Ti4	293.7(5)		2Bi2	346.4(1)
	2Ti1	307.4(5)		2Ti1	297.1(4)		1Bi3	352.7(1)
	1Ti3	371.5(5)		1Ti3	312.2(6)		2Bi1	376.8(1)
Ti2:	2Bi1	284.8(1)		1Bi1	334.1(1)		2Bi1	387.7(1)
	4Bi2	293.1(1)		2Bi1	338.9(1)	Bi3:	4Ti1	294.5(4)
	4Ti1	301.7(4)		2Bi2	376.8(1)		4Bi2	352.7(1)
	2Ti3	367.7(1)		2Bi2	387.7(1)		8Bi1	399.9(1)
Ti3:	4Bi1	312.2(6)		2Bi3	399.9(1)			
	4Bi2	314.4(6)						
	4Ti2	367.7(1)						
	1Ti4	368(1)						
	1Ti4	370(1)						
	4Ti1	371.5(5)						

^{a} All distances shorter than 400 pm are listed.

FIG. 2. Coordination polyhedra in the structure of Ti$_8$Bi$_9$. All atoms at distances shorter than 400 pm are shown. The site symmetries of the central atoms are indicated in parentheses.

both titanium and hafnium. Differences in the Mulliken overlap populations of these metals may also play a role (18, 19).

In the structure of Ti$_8$Bi$_9$ all atoms have high coordination numbers (Fig. 2), as is typical for intermetallic compounds. The titanium atoms occupy four different atomic sites. The Ti1 and Ti2 atoms have both six bismuth and six titanium neighbors together forming distorted icosahedra.

The certainly more strongly bonded six bismuth neighbors of both titanium atoms form distorted octahedra. Nevertheless, the icosahedra of Ti and Bi atoms around the Ti1 and Ti2 atoms are dissimilar; e.g., the icosahedron around a Ti1 atom has one triangular face formed only by titanium (Ti1) atoms and two triangular faces formed only by bismuth atoms, while the icosahedron surrounding the Ti2 atom again has two faces formed only by bismuth atoms, but no face formed only by titanium atoms.

In contrast, the Ti3 and Ti4 atoms have both eight bismuth neighbors, forming distorted square antiprisms. From a geometric point of view these coordinations are completed by titanium atoms; however, the Ti–Ti distances in the coordination polyhedra of the Ti3 and Ti4 atoms are all greater than 367 pm. Hence, only very weak Ti–Ti bonds at best can be assumed for the Ti3 and Ti4 atoms.
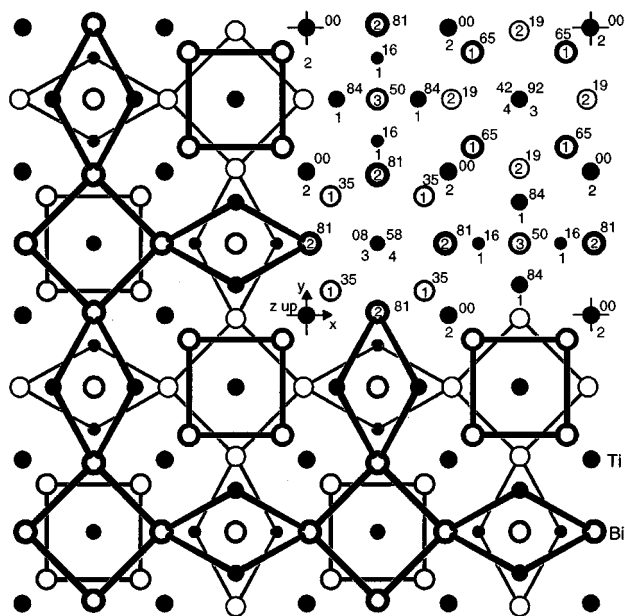
On the other hand, some titanium-titanium bonding must be present for the Ti1 and Ti2 atoms, as can be

FIG. 1. Crystal structure of Ti$_8$Bi$_9$. Atoms at approximately the same height of the projection direction are connected by heavy ($z = 0.65$–0.84) and thin lines ($z = 0.16$–0.35), respectively. Single-digit numbers correspond to the atom designations, two-digit numbers indicate the heights of the atoms in hundredths.

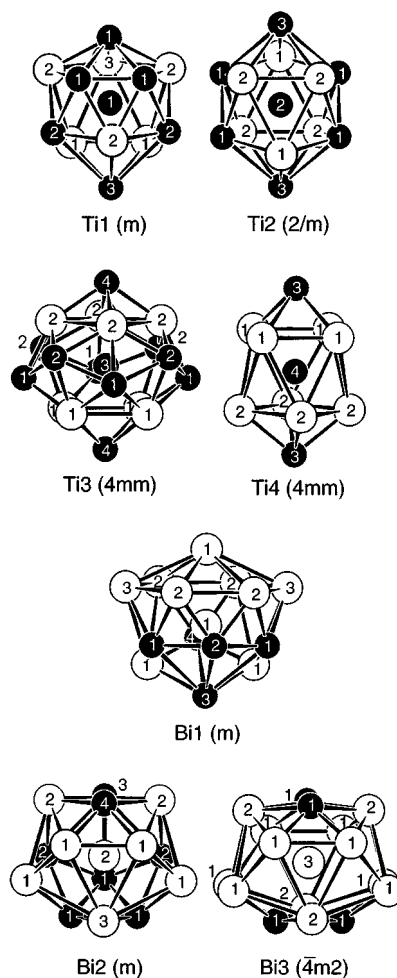concluded by a comparison of the Ti–Bi distances of the four different titanium atoms, considering the differing coordination numbers of these atoms. The Ti–Bi distances cover the relatively narrow range between 282 and 314 pm. The average Ti–Bi bonds are 297.6, 290.3, 313.3, and 296.1 pm for the Ti1, Ti2, Ti3, and Ti4 atoms, respectively. These average distances do not properly reflect the different bismuth coordinations of the four titanium atoms. The average Ti–Bi bond lengths of the Ti1 and Ti2 atoms with six bismuth neighbors should be smaller than the average Ti–Bi distances for the Ti3 and Ti4 atoms with eight bismuth neighbors. This long known empirical rule is especially violated by the Ti1 and Ti4 atoms, where the average Ti1–Bi bond distance of 297.6 pm is even greater than the average Ti4–Bi distance of 296.1 pm. This can only be rationalized if the titanium atoms in the coordination shell of the Ti1 atoms are also counted as bonded neighbors. The Ti1 atoms have five titanium neighbors at 293 (1×), 302 (2×), and 307 pm (2×). These distances are all only 5% or less greater than two times the metallic radius of a titanium atom for the coordination number 12 of 2 × 146.2 pm = 292.4 pm (20). Since the Ti1–Ti2 bonds of 302 pm are common to both titanium atoms, Ti–Ti bonding must also be assumed for the Ti2 atoms.

The three different kinds of bismuth atoms Bi1, Bi2, and Bi3 in Ti$_8$Bi$_9$ are coordinated by five, seven, and four titanium atoms at average distances of 297.0, 299.4, and 294.5 pm, respectively. These values properly reflect the different coordination numbers. Neverthess, some bismuth–bismuth bonding certainly is also present. The Bi–Bi distances almost continuously cover the range between 334.1 and 399.9 pm. These values might be compared to the Bi–Bi distances of 307.2 (3×) and 352.9 pm (3×) in elemental bismuth (21). In a very (too) simple bonding description of elemental bismuth one might ascribe classical two-electron bonds to each of the three short Bi–Bi interactions at 307.2 pm, and van der Waals bonds to the three Bi–Bi interactions with the larger distance of 352.9 pm. However, certainly the bonding interactions at 352.9 pm are stronger than van der Waals bonds; otherwise bismuth would show a preferred cleavage like graphite, which is not the case. Hence, the Bi–Bi distances of 334, 339, 346, and 353 pm in Ti$_8$Bi$_9$ might all be considered as bonding distances, and therefore all three different kinds of bismuth atoms form bismuth–bismuth bonds. However, these bonds are weak, certainly all with bond orders of less than one, since the Bi–Bi distances in Ti$_8$Bi$_9$ are all considerably greater than the short bond distances of 307.2 pm in elemental bismuth.

We thus realize that Ti$_8$Bi$_9$ has strong bismuth–titanium and weak titanium–titanium as well as weak bismuth-bismuth bonds (Fig. 3). These near-neighbor interactions might be compared with the near-neighbor interactions in the series of homologous compounds TiPn (Pn = P, As, Sb) TiP with TiAs type structure (22), TiAs with TiAs type (23)
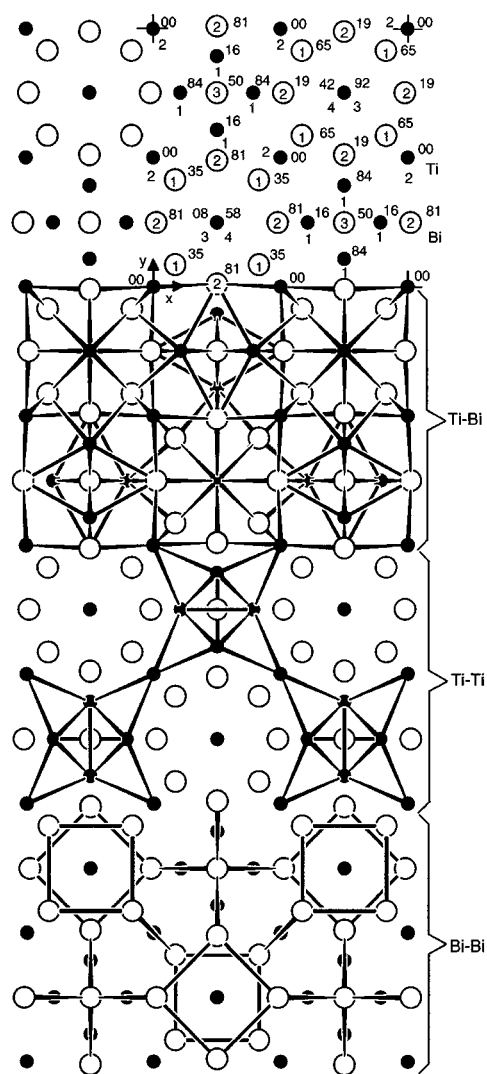

FIG. 3. Bonding interactions in the structure of Ti$_8$Bi$_9$. In the upper part of the drawing the atom labels and the heights of the atoms are indicated in a way similar to that of Fig. 1. In lower parts of the figure the short Ti–Bi, Ti–Ti, and Bi–Bi distances are indicated.

and NiAs type structures (24), and TiSb with NiAs type structure (25). In these compounds the titanium atoms all have six pnictogen neighbors and some titanium–titanium bonding with the shortest Ti–Ti distances varying between 307.5 pm for the NiAs type structure of TiAs and 320.5 pm for the TiAs type structure of this composition. The pnictogen atoms all have six titanium and no pnictogen neighbors. The shortest Pn–Pn distances in these compounds of 350 pm (P–P), 364 pm (As–As), and 393 pm (Sb–Sb) are certainly all nonbonding. In contrast, Ti$_8$Bi$_9$ has some Bi–Bi bonding, as discussed in the preceeding paragraph, with the shortest Bi–Bi distance being 334 pm. This clearly demonstrates the more metallic character of bismuth with its tendency for higher coordination numbers.

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