Bi₂AuO₅ and Bi₄Au₂O₉, Two Novel Ternary Oxoaurates

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Bi_2AuO_5 and Bi_4AuO_9, the first ternary bismuth aurates, have been synthesized applying hydrothermal conditions (aqueous solution of KOH as a mineralizer). Bi_2AuO_5 crystallizes in space group $P4/ncc$ with four formula units in the unit cell of the dimensions $a = 8.6703(4)$ Å, $c = 6.0301(3)$ Å. The structure consists of square planar AuO_4 units which are stacked to form columns parallel to [001]. They are linked to build a three-dimensional network by eightfold-coordinated bismuth atoms. $Bi_4Au_2O_9$ crystallizes in the orthorhombic crystal system; $Pcab$, $a = 5.889(1)$ Å, $b = 8.847(2)$ Å, $c = 34.674(6)$ Å, $Z = 8$. The structure can be derived from Bi_2AuO_5 by quadrupling the a axis and removing half of the oxygen atom O(2). The structural relations of both compounds to Bi_2CuO_4 will be discussed. © 1996 Academic Press, Inc.

INTRODUCTION

Up to now, only a few ternary bismuth oxides with cations of noble metals are known. There are reports on $Bi_2Ru_2O_7$, $Bi_2Ir_2O_7$ (1), $Bi_2Pt_2O_7$ (2), and $Bi_2Rh_2O_{6.8}$, which crystallize in a pyrochlor type of structure, as well as on $BiRhO_3$ (3), which forms a perovskite structure. Recently, the syntheses of the silver bismuthates Ag_3BiO_3 (4), Ag_5BiO_4 (4), and $Ag_{25}Bi_3O_{18}$ (5) were achieved by application of high oxygen pressure. $AgBiO_3$, which is formed by ion exchange of $KBiO_3$ (6), was synthesized for the first time in 1941. Apart from these compounds, in which the noble metal cation is coordinated octahedrally or linearly by oxygen, there are two more compounds Bi_2MO_4 (M = Pd, Cu) (7–10) which contain Pd or Cu in a square planar coordination. So far, ternary oxides with bismuth and gold have not been known. Since the d^8 configurated ion Au^{3+} also prefers a square planar coordination it should be possible to synthesize a compound of a composition like Bi_2AuO_{4+x}, in which the bismuth cuprate structure is preserved. The oxygen ion necessary for the charge neutrality could be accomodated at spacings within the Bi_2CuO_4 type of structure.

EXPERIMENTAL

Syntheses, starting materials. $Bi_4Au_2O_9$ and Bi_2AuO_5 were synthesized at hydrothermal conditions applying high oxygen pressures. Amorphous Bi_2O_5 and $Au_2O_3 \cdot xH_2O$ (x = 2–3) were used as starting materials. $Au_2O_3 \cdot 2H_2O$ was prepared as described in (11) from elemental gold (Degussa, 99.99%). The content of gold was proven by thermal decomposition to be 82.14% (calculated for $Au_2O_3 \cdot 2H_2O$: 82.42%). In order to prepare Bi_2O_5, first Bi_2O_3 (Merck, p.a.) was oxidized with bromine (Merck, p.a.) in a saturated aqueous solution of NaOH to get $NaBiO_3$ which was converted to Bi_2O_5 as described by Scholder and Stobbe (6). The bismuth content was determined by titration of a solution of the bismuth oxide in nitric acid with Titriplex and pyrogallolred as indicator (12) (found, 80.3%; calculated, 83.93%). Bi_2O_5 and $Au_2O_3 \cdot 2H_2O$ were mixed intimately and placed in a gold tube. Because the gold tube was always attacked during the reaction the amount of $Au_2O_3 \cdot xH_2O$ in the starting mixture has to be ca. 3% below the precise value. As a mineralizer 0.3 ml of a 40% aqueous solution of KOH (Aldrich, 99.99%) was added. The tube was closed permeable to gas and transferred into a steel autoclave. The reaction to $Bi_4Au_2O_9$ took place at 400°C and an oxygen pressure of 3 kbar. In order to obtain Bi_2AuO_5, the conditions were changed to 280°C and to a pressure of 5 kbar. At intermediate temperatures and pressures both phases formed simultaneously. After a reaction period of 3 days the autoclave was cooled to room temperature. To remove KOH the crude product was washed with water and subsequently dried in an desiccator over P_4O_{10} for 3 days.

Under these reaction conditions, powders of Bi_2AuO_5 and single crystals of $Bi_4Au_2O_9$ were obtained. In order to prepare single crystals of Bi_2AuO_5, the bismuth(V) oxide was covered with a surplus of colloidal gold (11) and treated as described above. Impurities other than α-Bi_2O_3 and elemental gold could not be detected.

Structure determinations. For X-ray structure determinations crystals of Bi_2AuO_5 (size: 0.021 × 0.021 × 0.0498 mm) and $Bi_4Au_2O_9$ (size: 0.481 × 0.011 × 0.003 mm) were

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TABLE 1
Crystal Data and Structure Refinement for Bi_2AuO_5 and $Bi_4Au_2O_9$

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Formula	Bi_2AuO_5	$Bi_4Au_2O_9$
Formula weight (g · mol^{-1})	694.93	1373.85
Space group	$P4/ncc$ (No. 130)	$Pcab$ (No. 61)
Unit cell dimensions (Å)	$a = 8.6703(4)$	$a = 5.889(1)$
	$b = 8.6703(4)$	$b = 8.847(2)$
	$c = 6.0301(3)$	$c = 34.674(6)$
Crystal size (mm)	$0.0166 \times 0.0166 \times 0.0498$	$0.4815 \times 0.0110 \times 0.0034$
Volume (Å^3)	453.31(4)	1807.0(2)
Z	4	8
D_{calc} (g · cm^{-3})	10.183	10.103
μ Mo$K\alpha$ (cm^{-1})	1096.5	1100.45
$F(000)$	1140	4496
Theta range for data collection [°]	$3.32 \leq \theta \leq 35.02$	$1.17 \leq \theta \leq 29.98$
Index ranges	$-14 \leq h \leq 4, -13 \leq k \leq 14,$ $-9 \leq l \leq 9$	$0 \leq h \leq 8, -8 \leq k \leq 12,$ $-48 \leq l \leq 48$
No. of reflections measured	3807	6840
No. of unique reflections	496 [R(int) = 0.1042]	2632 [R(int) = 0.0688]
Corrections	Lorentz-Polarization numerical absorption	Lorentz-Polarization numerical absorption
Parameters	21	137
$R1$	7.32	4.51
w$R2$	17.03	12.13
Extinction coefficient	0.0015(5)	0.00010(2)

selected. From film methods the space groups $P4/ncc$ and $Pcab$ were derived for Bi_2AuO_5 and $Bi_4Au_2O_9$, respectively. Room temperature intensity data collections were carried out on an Enraf Nonius CAD4 automatic four-circle diffractometer (graphite-monochromated Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å). Crystal data and experimental details of the structure determinations are listed in Table 1. The cell parameters used in all calculations were determined from X-ray powder patterns (c.f. Table 2, Stoe-Stadi P diffractometer, germanium monochromator on the primary beam, Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å), Si as an external standard) using Stoe-Stadi P software.

For data reduction the program CADSHEL (13) was used. A numerical absorption correction (HABITUS (14)) was applied to both data sets. Neutral-atom scattering factors were taken from the "International Tables for X-Ray Crystallography" (15). The localization of the heavy atoms was achieved by Patterson methods using the program SHELXS-86 (16). Determination of the oxygen atom positions and final structure refinements were carried out by difference Fourier synthesis and least squares methods by SHELXL-93 (17). The structure plots were prepared using KPLOT (18).

Analyses. The cation ratio in the crystals was determined by energy dispersive X-ray analyses using an electron microscope (Zeiss DSM 940) equipped with EDX (EDAX PV9800). Difference thermal and thermogravimetric analyses were performed on a Netsch STA 429

(heating rate, 5 K/min; reference, high purity α-Al_2O_3; Ar atmosphere). The decomposition products were identified by X-ray powder investigations.

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RESULTS

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$Bi_4Au_2O_9$ and Bi_2AuO_5, two novel ternary bismuth–gold oxides, were obtained by hydrothermal reaction of amorphous Bi_2O_5 and $Au_2O_3 \cdot 2H_2O$ applying high oxygen pressures. $Bi_4Au_2O_9$ forms red, needle shaped crystals. Bi_2AuO_5 crystallizes as black, tetragonal prisms which highly tend to form twins. The X-ray powder diffractogram of both substances show additional peaks of low intensity from bismuth oxide (α-Bi_2O_3). Both substances are insensitive to air, humidity, and exposure to daylight. The cation composition was proven by EDX analyses ($Bi_4Au_2O_9$, Bi : Au $= 2 : 0.99$; Bi_2AuO_5, Bi : Au $= 2 : 1.01$; calculated as a mean of 10 spot analyses). The content of potassium was below the limit of the detectibility of 0.3%. The substances decompose at 673 K ($Bi_4Au_2O_9$) and 586 K (Bi_2AuO_5) to α-Bi_2O_3 and elemental gold. Thermogravimetric analyses of a sample of Bi_2AuO_5, which showed only slight impurities of elemental gold gave a loss of oxygen of 3.99 wt% (calculated for Bi_2AuO_5, 4.6 wt%). This corresponds to an empirical formula of $Bi_2AuO_{4.73}$.

The results of the crystal structure determination

TABLE 2
X-Ray Pattern of Bi_2AuO_5 and $Bi_4Au_2O_9$, d (Å), $\lambda = 1.54056$ Å, $T = 273$ K

		Bi_2AuO_5						$Bi_4Au_2O_9$			
h	k	l	I_0/I_{max}	d_0	d_c	h	k	l	I_0/I_{max}	d_0	d_c
1	1	0	8.4	6.1303	6.1308	0	1	4	9.4	6.1996	6.1928
2	1	1	100.0	3.2606	3.2614	1	1	1	1.8	4.8485	4.8540
2	2	0	15.5	3.0653	3.0654	0	1	6			4.8393
0	0	2	8.6	3.0143	3.0151	0	2	2	4.6	4.2878	4.2865
1	0	2	17.0	2.8473	2.8478	1	1	6	2.6	3.7417	3.7388
3	1	0	46.5	2.7417	2.7418	1	2	4	100.0	3.2762	3.2750
1	1	2	15.5	2.7052	2.7056	1	1	8	77.2	3.2502	3.2477
2	0	2	16.6	2.4750	2.4753	0	2	8	17.1	3.0997	3.0964
2	1	2	9.9	2.3799	2.3802	2	0	0	26.0	2.9442	2.9445
3	2	1	2.2	2.2336	2.2337	1	2	7	3.5	2.8788	2.8788
4	0	0	0.4	2.1675	2.1676	2	0	3	4.4	2.8516	2.8534
3	0	2	2.6	2.0864	2.0864	2	1	0	54.2	2.7936	2.7938
3	3	0	2.4	2.0437	2.0436	0	3	4			2.7921
3	1	2	4.2	2.0285	2.0285	0	1	12	32.7	2.7511	2.7474
4	1	1	15.9	1.9857	1.9856	0	3	5	15.1	2.7102	2.7141
4	2	0	11.2	1.9389	1.9387	2	0	5			2.7104
3	2	2	5.5	1.8800	1.8800	2	1	4	29.7	2.6594	2.6592
2	1	3	14.9	1.7844	1.7845	0	3	6	3.4	2.6237	2.6270
4	0	2	9.0	1.7600	1.7600	2	0	6			2.6237
4	1	2	4.0	1.7248	1.7248	1	0	12	4.6	2.5916	2.5947
5	1	0	1.8	1.7005	1.7004	2	1	5			2.5915
3	3	2	14.1	1.6916	1.6916	1	3	3	3.4	2.5699	2.5709
5	2	1	8.9	1.5557	1.5555	0	2	11			2.5676
4	4	0	2.7	1.5329	1.5327	0	0	14	3.6	2.4777	2.4774
4	3	2	3.5	1.5035	1.5032	1	2	10			2.4764
5	3	0	4.0	1.4866	1.4869	2	2	0	19.5	2.4513	2.4511
5	1	2	1.6	1.4811	1.4811	0	3	8	16.4	2.4362	2.4385
1	1	4	1.7	1.4638	1.4639	2	0	8			2.4358
4	1	3	2.9	1.4530	1.4530	2	1	7			2.4336
6	0	0	3.9	1.4451	1.4451	1	3	6	8.1	2.3989	2.3991
2	0	4	1.9	1.4238	1.4239	2	2	3			2.3978
5	2	2	2.2	1.4202	1.4202	0	0	15	4.1	2.3117	2.3123
6	0	1	1.3	1.4051	1.4053	2	2	5			2.3111
2	1	4			1.4051	2	1	9	4.3	2.2614	2.2620
6	2	1	0.4	1.3367	1.3368	2	2	6	3.7	2.2543	2.2567
3	0	4			1.3366	1	3	8			2.2530
5	4	1	3.1	1.3212	1.3212	1	2	12	3.0	2.2399	2.2381
3	1	4			1.3210	0	4	0	2.3	2.2130	2.2119
6	0	2	1.1	1.3031	1.3031	1	1	14			2.2111
6	1	2	0.8	1.2887	1.2886	2	2	7	1.8	2.1956	2.1970
3	2	4	1.0	1.2773	1.2773	0	4	2			2.1941
5	2	3	3.0	1.2566	1.2566	0	4	3	2.2	2.1722	2.1725
6	2	2	1.7	1.2480	1.2480	1	3	10	1.9	2.1007	2.0992
7	0	0	1.7	1.2377	1.2386	2	3	1	2.3	2.0803	2.0800
4	0	4			1.2376	2	3	2	4.6	2.0666	2.0688

(atomic parameters, equivalent thermal parameters, and interatomic distances) are documented in Tables 3–6.[2]

The refinement of the anisotropic temperature factors for O(2) for Bi_2AuO_5 led to the extremely high value of 0.5 Å^2 for U_{11} and U_{22}, indicating that this site may be occupied only partly, or that the crystal might be a

[2] Further details of the structure determination have been deposited as supplementary publication No. CSD-59143 for Bi_2AuO_5 and $Bi_4Au_2O_9$. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

TABLE 3
Atomic Coordinates and Equivalent Thermal Parameters[a] (Å^2) for Bi_2AuO_5

Atom	Wyckoff notation	x	y	z	U_{eq}[a]
Bi(1)	8f	0.09201(0)	0.9080(1)	0.25	0.023(1)
Au(1)	4c	0.25	0.25	0.0861(3)	0.013(1)
O(1)	16f	0.158(2)	0.351(3)	0.095(4)	0.025(4)
O(2)	4a	0.25	0.75	0.0	0.05(1)

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

TABLE 4
Atomic Coordinates and Equivalent Thermal Parameters[a] [Å^2] for Bi$_4$Au$_2$O$_9$

Atom	Wyckoff notation	x	y	z	U_{eq}[a]
Bi(1)	8c	0.7723(2)	0.5809(1)	0.1029(1)	0.008(1)
Bi(2)	8c	−0.2735(2)	0.3817(1)	0.2298(1)	0.009(1)
Bi(3)	8c	0.2491(2)	0.5725(1)	0.5249(1)	0.009(1)
Bi(4)	8c	0.2678(2)	0.3988(1)	0.1528(1)	0.009(1)
Au(1)	8c	0.1019(2)	0.2489(1)	0.0600(1)	0.007(1)
Au(2)	8c	0.9283(2)	0.7575(1)	0.1821(1)	0.006(1)
O(1)	8c	0.093(3)	0.361(2)	0.0092(5)	0.007(3)
O(2)	8c	0.123(3)	0.456(2)	0.0830(5)	0.008(3)
O(3)	8c	0.535(3)	0.235(2)	0.1916(4)	0.012(3)
O(4)	8c	0.903(3)	0.680(2)	0.2365(5)	0.010(3)
O(5)	8c	0.947(3)	0.846(2)	0.1290(5)	0.010(3)
O(6)	8c	0.896(3)	0.965(2)	0.2023(5)	0.008(3)
O(7)	8c	0.927(3)	0.548(2)	0.1575(5)	0.008(3)
O(8)	8c	0.143(3)	0.146(2)	0.1110(5)	0.010(3)
O(9)	8c	0.090(3)	0.044(2)	0.0340(5)	0.010(3)

^{a} $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

superposition of two orthorhombic individuals. Alternating refinements of the occupation factor and the anisotropic temperature factors for O(2) were made, but resulted in only slightly improved temperature factors with an extremely high standard deviation. An attempt to solve the problem by using a program for refinement of twined crystals failed. However, a restriction of the data set to reflections between $d = 0.69$ Å and $d = 1.39$ Å (observ./parameter = 15.2:1) leads to much more realistic values ($U_{11} = U_{22} = 0.05(2)$).

DISCUSSION

In the crystal structure of Bi$_2$AuO$_5$ gold occupys a special position of site symmetry 4. It is coordinated by four oxygen atoms forming a regular square planar unit, confirming the oxidation state of 3+ for gold. The Au–O bond length is 2.00(2) Å, which matches those found in other ternary aurates. The AuO$_4$ units are stacked along [001], and they are twisted to each other by 22.5°. The resulting isolated columns of AuO$_4$ units are connected by bismuth atoms in such a way that each Bi atom connects four AuO$_4$ groups of two different columns. This situation is shown in Fig. 1, were a projection onto the ab plane of the structure is depicted. For the Bi atoms an eightfold coordination of oxygen atoms results. The coordination polyhedron can be described as a distorted tetragonal antiprism as shown in Fig. 2. The partial structure of the bismuth atoms consists of chains of edge sharing tetrahedra. Each tetrahedron of Bi atoms is centered by oxygen. Thus the structure may be de-

scribed as an arrangement of alternating chains of Bi$_4$ tetrahedra and columns of AuO$_4$ groups.

The crystal structure of Bi$_4$Au$_2$O$_9$ can be derived from that of Bi$_2$AuO$_5$ by quadrupling the a axis and removing half of the oxygen atoms in the centers of the bismuth tetrahedra. The resulting arrangement is shown in Fig. 3. The distribution of occupied and empty tetrahedra and the kind of stacking of the AuO$_4$ groups (cf. Fig. 4) leads to a distortion of the original structure, which is also reflected by the first coordination spheres. For the gold atoms the average Au–O distances remain nearly unchanged (dAu–O = 2.01 Å), whereas the individual bond lengths range from 2.00(2) to 2.03(2) Å for Au(1) and 1.98(2) to 2.04(2) Å for Au(2). The sum of the observed O–Au–O

TABLE 5
Selected Bond Lengths (Å) and Angles (°) for Bi$_4$Au$_2$O$_9$

Au(1)–O(8)	2.00(2)	O(1)–Au(1)–O(2)	84.2(6)
Au(1)–O(2)	2.00(2)	O(1)–Au(1)–O(9)	92.7(7)
Au(1)–O(1)	2.03(2)	O(2)–Au(1)–O(8)	93.4(6)
Au(1)–O(9)	2.03(2)	O(8)–Au(1)–O(9)	89.5(7)
Au(2)–O(6)	1.98(2)	O(4)–Au(2)–O(6)	88.8(6)
Au(2)–O(5)	2.00(2)	O(4)–Au(2)–O(7)	94.7(7)
Au(2)–O(4)	2.01(2)	O(5)–Au(2)–O(6)	88.1(7)
Au(2)–O(7)	2.04(2)	O(5)–Au(2)–O(7)	88.3(7)
Bi(1)–O(7)	2.12(2)	O(7)–Bi(1)–O(8)	84.9(6)
Bi(1)–O(8)	2.16(2)	O(5)–Bi(1)–O(2)	168.1(6)
Bi(1)–O(5)	2.21(2)	O(7)–Bi(1)–O(5)	69.9(5)
Bi(1)–O(2)	2.44(2)	O(5)–Bi(1)–O(9)	139.2(5)
Bi(1)–O(5)	2.72(2)	O(8)–Bi(1)–O(9)	67.3(6)
Bi(1)–O(9)	2.84(2)	O(8)–Bi(1)–O(5)	85.2(6)
Bi(2)–O(3)	2.17(2)	O(3)–Bi(2)–O(4)	94.5(5)
Bi(2)–O(4)	2.30(2)	O(4)–Bi(2)–O(6)	66.9(5)
Bi(2)–O(4)	2.38(2)	O(6)–Bi(2)–O(6)	117.9(4)
Bi(2)–O(3)	2.47(2)	O(6)–Bi(2)–O(3)	72.2(5)
Bi(2)–O(6)	2.56(2)	O(7)–Bi(2)–O(4)	146.0(5)
Bi(2)–O(6)	2.66(2)	O(4)–Bi(2)–O(3)	99.3(5)
Bi(2)–O(4)	2.84(1)	O(3)–Bi(2)–O(3)	78.7(5)
		O(6)–Bi(2)–O(4)	79.5(4)
Bi(3)–O(1)	2.16(2)	O(1)–Bi(3)–O(9)	81.5(6)
Bi(3)–O(9)	2.26(2)	O(1)–Bi(3)–O(2)	72.7(6)
Bi(3)–O(9)	2.27(2)	O(9)–Bi(3)–O(1)	156.2(6)
Bi(3)–O(2)	2.39(2)	O(1)–Bi(3)–O(2)	144.0(5)
Bi(3)–O(1)	2.42(2)	O(1)–Bi(3)–O(9)	66.8(5)
Bi(3)–O(1)	2.96(1)	O(9)–Bi(3)–O(1)	100.5(5)
Bi(4)–O(6)	2.23(2)	O(6)–Bi(4)–O(7)	86.1(6)
Bi(4)–O(3)	2.25(2)	O(3)–Bi(4)–O(7)	75.0(6)
Bi(4)–O(7)	2.41(2)	O(6)–Bi(4)–O(3)	71.9(6)
Bi(4)–O(3)	2.53(2)	O(3)–Bi(4)–O(3)	76.2(3)
Bi(4)–O(2)	2.62(2)	O(7)–Bi(4)–O(2)	71.7(5)
Bi(4)–O(5)	2.62(2)	O(6)–Bi(4)–O(5)	69.0(5)
Bi(4)–O(8)	2.67(2)	O(2)–Bi(4)–O(5)	71.0(5)
Bi(4)–O(8)	2.76(2)	O(3)–Bi(4)–O(8)	71.9(5)
		O(5)–Bi(4)–O(8)	67.9(5)
		O(3)–Bi(4)–O(8)	74.2(6)
		O(8)–Bi(4)–O(8)	79.3(4)

TABLE 6
Selected Bond Lengths (Å) and Angles (°) for Bi₂AuO₅

Au(1)–O(1)	4 × 2.02(2)	O(1)–Au(1)–O(1)	4 × 89.97(4)
		O(1)–Au(1)–O(1)	2 × 177(2)
Bi(1)–O(1)	2 × 2.34(3)	O(1)–Bi(1)–O(2)	68.7(9)
Bi(1)–O(1)	2 × 2.42(2)	O(2)–Bi(1)–O(1)	63.8(5)
Bi(1)–O(2)	2 × 2.455(1)	O(1)–Bi(1)–O(1)	68.7(9)
Bi(1)–O(1)	2 × 2.69(2)	O(1)–Bi(1)–O(1)	75.4(8)
		O(1)–Bi(1)–O(1)	85.8(5)
		O(1)–Bi(1)–O(2)	89.3(5)
		O(2)–Bi(1)–O(2)	75.76(4)
		O(1)–Bi(1)–O(1)	80.2(2)
Bi(1)–Bi(1)	3.7665(1)		
Bi(1)–Au(1)	3.4133(8)		
Au(1)–Au(1)	3.0150(1)		

TABLE 7
Anisotropic Displacement Parameters (Å²) for Bi₂AuO₅

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	0.017(1)	0.017(1)	0.024(1)	0.001(1)	0.001(1)	−0.008(1)
Au(1)	0.008(1)	0.008(1)	0.011(1)	0.0	0.0	0.0
O(1)	0.03(1)	0.019(9)	0.03(1)	−0.007(1)	−0.01(1)	0.017(9)
O(2)	0.05(2)	0.05(2)	0.05(3)	0.0	0.0	0.0

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

TABLE 8
Anisotropic Displacement Parameters (Å²) for Bi₄Au₂O₉

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi(1)	0.010(1)	0.005(1)	0.009(1)	0.000(1)	0.000(1)	0.000(1)
Bi(2)	0.011(1)	0.005(1)	0.012(1)	−0.001(1)	−0.001(1)	−0.001(1)
Bi(3)	0.010(1)	0.006(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)
Bi(4)	0.011(1)	0.006(1)	0.011(1)	−0.002(1)	0.000(1)	−0.001(1)
Au(1)	0.008(1)	0.004(1)	0.009(1)	0.000(1)	0.000(1)	0.000(1)
Au(2)	0.007(1)	0.003(1)	0.008(1)	0.000(1)	0.000(1)	0.000(1)
O(1)	0.006(4)	0.007(4)	0.009(4)	0.001(3)	0.004(3)	0.001(3)
O(2)	0.010(5)	0.007(4)	0.008(4)	−0.001(3)	−0.001(3)	0.000(3)
O(3)	0.012(5)	0.012(5)	0.013(4)	−0.002(4)	0.000(4)	−0.002(4)
O(4)	0.010(5)	0.010(4)	0.011(4)	−0.001(3)	−0.003(3)	0.003(3)
O(5)	0.11(5)	0.010(4)	0.010(4)	−0.002(3)	−0.001(4)	−0.002(4)
O(6)	0.011(5)	0.007(4)	0.006(4)	−0.001(3)	0.000(1)	0.002(3)
O(7)	0.011(5)	0.003(4)	0.010(4)	0.001(3)	0.004(4)	0.000(3)
O(8)	0.011(5)	0.007(4)	0.011(4)	−0.002(3)	0.000(4)	0.000(3)
O(9)	0.009(5)	0.010(4)	0.011(4)	0.000(3)	0.000(3)	−0.001(4)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.
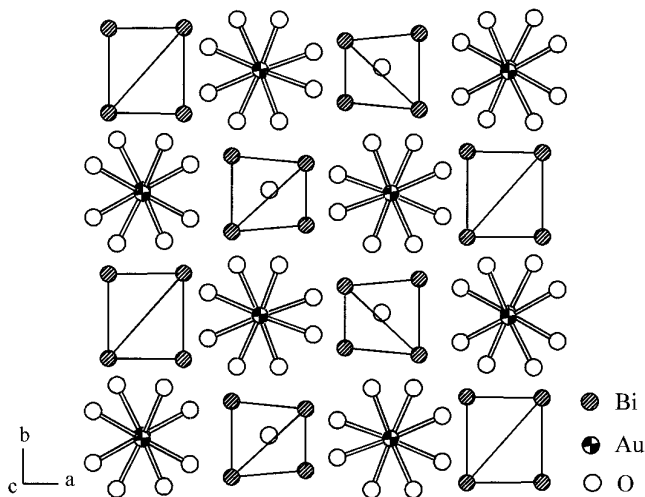

FIG. 1. Projection of the crystal structure of Bi₂AuO₅ along the *c* axis. The bonds from Bi to O(2) are not drawn.
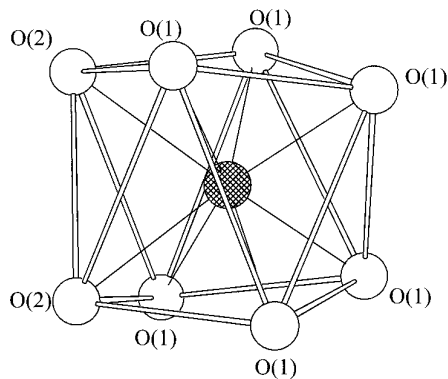
FIG. 2. The coordination of Bi in Bi₂AuO₅.

FIG. 3. Alternating stacking of chains of Bi₄ tetrahedra and AuO₄ columns in Bi₄Au₂O₉.

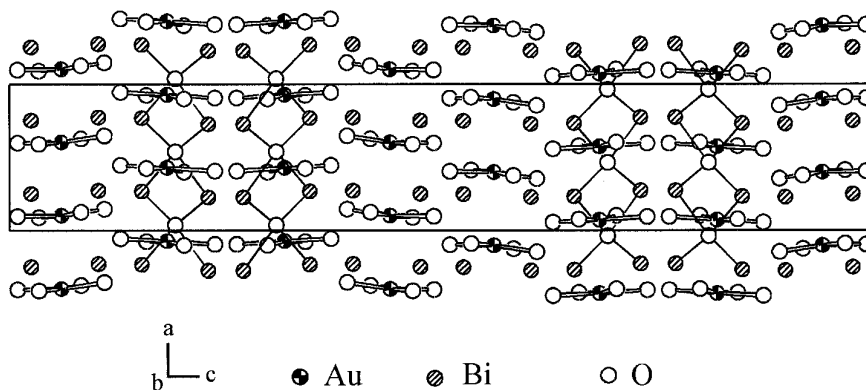**FIG. 4.** View along [010] upon the unit cell of $Bi_4Au_2O_9$.

angles is 360° within the e.s.d.'s for both atoms. The plausi-
bility of the observed Au–O distances was checked by
a valence bond sum calculation (20) performed for both
atoms.[3] As a result values of 2.91 and 2.94 for Au(1) and
Au(2), respectively, were obtained. The smaller content
of oxygen compared to Bi_2AuO_5 causes a change in the
coordination of bismuth by oxygen atoms. Two of the four
crystallographically independent bismuth atoms are sur-
rounded by six oxygen atoms forming a distorted octahe-
dron. The coordination polyhedron of Bi(4) is still a tetrag-
onal antiprism, whereas Bi(2) is coordinated by seven
atoms to form a monocapped trigonal prism (cf. Fig. 5).
The individual Bi–O distances vary considerably which is
not unusual for tervalent bismuth. A valence bond sum
calculation for all Bi atoms gives values between 2.81
and 3.17.

The structures of Bi_2AuO_5 and $Bi_4Au_2O_9$ both belong
to the structure family of Bi_2CuO_4, which is completed
by Bi_2PdO_4 and $La_4Au_2O_9$ (21). The basic motif which is
common to all these structures is isolated columns of
square planar MO_4 units, which are twisted by 22.5°
against each other. Between these rows there are chains
of edge sharing M_4 tetrahedra. The main difference
between the individual members of this structure family
is the amount of occupation of the M_4 tetrahedra by
oxygen atoms. The borderline cases are Bi_2CuO_4 and
Bi_2PdO_4 with no tetrahedra occupied on the one hand,
and Bi_2AuO_5 where all Bi_4 tetrahedra are centered by
oxygen atoms on the other hand. In $Bi_4Au_2O_9$ and
$La_4Au_2O_9$, half of all M_4 polyhedra are centered, but
both structures differ in the ordered distribution of the
oxygen atoms over the tetrahedral interstices. In Bi_4
Au_2O_9 every second chain of Bi_4 tetrahedra is not occu-
pied whereas in $La_4Au_2O_9$ there is a regular occupation
of every second La_4 tetrahedron in each chain.

[3] Bond valence parameter for gold from (19).
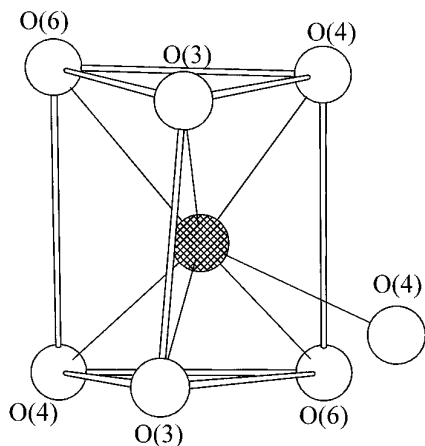
FIG. 5. Coordination polyhedron of Bi(2) in $Bi_4Au_2O_9$.

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