

Crystal Structure of Tetragonal Bismuth Arsenate, BiAsO_4

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The complete crystal structure of the tetragonal form of bismuth arsenate has been determined by X-rays. The crystal has the scheelite structure. The body-centered cell, containing four molecules, has the following dimensions:

$$a = 5.08 \pm 0.02 \text{ \AA}, \quad c = 11.70 \pm 0.02 \text{ \AA}, \quad c/a = 2.30.$$

The calculated density is 7.6 g.cm^{-3}

The space group is $C_{4h}^6-I4_1/a$. The arsenic and bismuth atoms are in fourfold special positions (*a*) and (*b*) of the space group, while the oxygen atoms are in the sixteenfold general positions (*f*). The oxygen parameters, given in fractions of the unit cell, are

$$x = 0.213, \quad y = 0.149, \quad z = 0.080.$$

Bismuth is in eight co-ordination, the average Bi-O distance being 2.54 \AA .

Introduction

Standard tables give the density of bismuth arsenate as 7.142 g.cm^{-3} and describe the crystals as monoclinic. These data are due to de Schulten (1903), who prepared the compound in 1903 and made an optical examination of microscopic crystals.

The present study of the crystal structure of bismuth arsenate by X-ray diffraction has shown that the compound has two commonly occurring structural modifications which coexist under ordinary conditions of crystallization. One phase is indeed monoclinic, as observed by de Schulten. The second phase is tetragonal, with a density about 3.5% greater than that of the monoclinic type. This paper deals with the crystal structure of the tetragonal form. A report on the monoclinic form and its isomorphs is in preparation.

Description of samples

Seven samples of precipitated bismuth arsenate were prepared for the purpose of this investigation by H. B. Evans, Chemistry Division, Metallurgical Laboratory, University of Chicago. The preparation of the several samples, as reported by Evans, followed the method of de Schulten, and differed among themselves only in the time allowed for digestion on a steam bath.

Preliminary optical examination of the precipitates revealed the presence of small but well-formed single crystals in four of the samples. These crystals were of distinctly different forms: one a tetragonal by-pyramid, the other a stout monoclinic prism. Though the single crystals observable in a given sample seemed all of one type, the powder diffraction patterns of the set of samples indicated mixtures of phases. The inter-

pretation of the complex patterns was achieved by means of cell constants obtained from single-crystal rotation and Weissenberg patterns of both crystal types. Two of the samples—both fine powders from rapid precipitation—proved to be single phases of the monoclinic modification. All of the others contained both phases in various proportions.

Inasmuch as the existence of the tetragonal form of bismuth arsenate was not known previous to this study, the method of preparation had been planned merely to promote crystal growth rather than to study the conditions which favor one or the other structural type. However, from the available evidence, all indications are that quickly precipitated bismuth arsenate crystallizes in the monoclinic form, while long digestion periods tend to produce the tetragonal form.

X-ray data

The diffraction data used in the structure analysis consisted of a single-crystal rotation diagram about the fourfold axis, three layer-line Weissenberg photographs perpendicular to the same axis, and a powder photograph taken in an 18 cm. diameter Bradley-type camera. In order to obtain a single-phase tetragonal pattern the powder rod was prepared from single crystals separated out from the original mixed sample under the microscope. Copper radiation filtered through nickel was used for all photographs.

The single-crystal data yielded preliminary cell constants and useful intensities for testing parameters. The final cell dimensions and the calculation of intensities are based on the powder pattern, as recorded in Table 1.

Table 1. Comparison of observed and calculated intensities for powder diffraction photograph of tetragonal BiAsO₄

The atomic scattering factors and the polarization factors used were obtained from *Internationale Tabellen*...

hkl	(sin θ)/λ		I	
	Calc.	Obs.	Obs.	Calc.
101	0.0276	0.0272	m	42.0
103	0.0624	0.0621	w	17.6
112	0.0638	0.0634	vs	197.2
004	0.0691	0.0691	m	36.1
200	0.0928	0.0924	m+	47.4
202	0.1102	—	Nil	0.4
114	0.1162	—	Nil	1.3
211, (2̄11)	0.1204	0.1195	m-	24.4
105	0.1322	0.1322	w	13.3
213, 2̄13	0.1552	0.1543	w-	18.0
204	0.1626	0.1619	s-	63.8
220	0.1856	0.1845	m-	26.0
222	0.2030	—	Nil	0.2
116	0.2034	0.2040	m+	38.2
301	0.2132	0.2125	vwv	6.9
215, (2̄15)	0.2250	0.2264	vwv	6.2
107	0.2366	0.2367	vwv	5.2
303	0.2480	—	m	{ 4.1
312, (3̄12)	0.2494	0.2489	m	{ 54.1
206	0.2498	—	Nil	0
224	0.2554	0.2556	w+	26.3
008	0.2790	0.2812	vwv	4.7
314, 3̄14	0.3018	—	—	0
321, 3̄21	0.3060	0.3052	w-	4.0
305	0.3178	0.3168	vwv	1.4
118	0.3254	—	—	0
217, 2̄17	0.3294	0.3288	vwv	3.1
323	0.3408	0.3405	w	3.1
226	0.3426	—	Nil	0.1
400	0.3716	—	m	{ 6.7
208	0.3718	0.3716	m	{ 16.4
109	0.3764	—	Nil	1.5
402	0.3890	—	m	{ 0.2
316, 3̄16	0.3890	0.3899	m	{ 28.3
411, 4̄11	0.3988	—	Nil	3.3
325, 3̄25	0.4106	0.4101	vwv	4.5
307	0.4222	—	Nil	0.8
413, 4̄13	0.4336	—	Nil	2.3
332	0.4350	0.4353	w	9.5
404	0.4414	0.4405	w	10.2
420, 4̄20	0.4640	—	w+	{ 10.6
228	0.4646	0.4649	w+	{ 9.2
219, 2̄19	0.4692	—	Nil	2.7
422, 4̄22	0.4814	—	Nil	0.2
1.1.10	0.4824	0.4825	w	9.2
334	0.4874	—	Nil	0
415, 4̄15	0.5034	0.5020	Tr.	2.6
318, 3̄18	0.5110	—	Nil	0
327, 3̄27	0.5150	0.5159	Tr.	3.0
406	0.5286	—	Nil	0
2.0.10	0.5288	—	Nil	0
424, 4̄24	0.5338	0.5325	w+	16.1
1.0.11	0.5508	—	Nil	0.9
309	0.5602	—	Nil	1.0
336	0.5746	0.5751	w	6.7
501	0.5844	0.5848	Tr.	0.7

Cell size and space group

Tetragonal bismuth arsenate has four molecules, BiAsO₄, in a body-centered cell of the following dimensions:

$$a = 5.08 \pm 0.02 \text{ \AA.}, \quad c = 11.70 \pm 0.02 \text{ \AA.}, \quad c/a = 2.30.$$

The X-ray calculated density is 7.61 g.cm.⁻³ No directly measured density is available for comparison.

The space group is $C_{4h}^6-I4_1/a$ as shown by the following characteristic absences of spectra:

- hkl absent unless $h+k+l$ is even;
- $hk0$ absent unless h and k are even;
- $00l$ absent unless $l=4n$.

Structure analysis

In addition to the sixteenfold general positions, the space group affords eightfold special positions in symmetry centers and in twofold axes, and two sets of fourfold positions in the fourfold inversion axes (*Internationale Tabellen*...).

The four arsenic atoms and the four bismuth atoms can only lie in special positions in the fourfold inversion axis. The sixteen oxygen atoms must be in general positions since the eightfold positions are eliminated by symmetry considerations.

The distribution of atoms in the structure is therefore the following:

- 4 As in (a) $0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}$; and each of these plus $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;
- 4 Bi in (b) $0, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{3}{4}$; and each of these plus $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;
- 16 O in (f) $x, y, z; \bar{x}, \bar{y}, z; x, \frac{1}{2}+y, \frac{1}{4}-z; \bar{x}, \frac{1}{2}-y, \frac{1}{4}-z; \bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; \bar{y}, \frac{1}{2}+x, \frac{1}{4}+z; y, \frac{1}{2}-x, \frac{1}{4}+z$; and each of these plus $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

Thus, only the determination of the three oxygen parameters is required to complete the structure. Because the scattering power of oxygen is roughly about one-fifth that of arsenic, and only one-fifteenth that of bismuth, the effect of the oxygen contribution on the observed intensity of reflections is in general small and often negligible.

The form of the structure amplitude expressions is conveniently given in Lonsdale's tables as follows, where

$$\theta_1 = (h-k)x + (h+k)y \quad \text{and} \quad \theta_2 = (h+k)x - (h-k)y.$$

For planes $2k+l=4n$:

$$A = 16 \cos \pi \theta_1 \cos \pi \theta_2 \cos 2\pi lz, \\ B = 0.$$

For planes $2k+l=4n+1$:

$$A = 8(\cos \pi \theta_1 \cos \pi \theta_2 \cos 2\pi lz - \sin \pi \theta_1 \sin \pi \theta_2 \sin 2\pi lz), \\ B = A.$$

For planes $2k+l=4n+2$:

$$A = 0, \\ B = -16 \sin \pi \theta_1 \sin \pi \theta_2 \sin 2\pi lz.$$

For planes $2k+l=4n+3$:

$$A = 8(\cos \pi \theta_1 \cos \pi \theta_2 \cos 2\pi lz + \sin \pi \theta_1 \sin \pi \theta_2 \sin 2\pi lz), \\ B = -A.$$

It may be seen that for planes of the type $2k+l=4n$, bismuth and arsenic are in phase. It follows that the oxygen contributions are negligible in comparison and only the natural decline of intensity with glancing angle is observable. For planes of the type $2k+l=4n+2$, the heavy atoms make no contribution. Only one plane (114) of this type was observed as a faint trace. Therefore the oxygen positions must be such as to contribute little to these planes. Actually, only planes of the type

$2k+l=4n+1$ or $4n+3$ are useful in fixing the oxygen parameters. Here the bismuth and arsenic contributions are of opposite signs, and the oxygen effect is appreciable in many cases, for instance in pairs such as $211(w-)$, $\bar{2}11(w)$; $213(m)$, $\bar{2}13(w)$ which were observed on Weissenberg photographs.

No attempt was made to determine the oxygen parameters directly from intensities; rather, the intensity data were used to verify assumptions based on predicated atomic distances and configuration. The configuration of the arsenate ion is well known to be tetrahedral. Since the arsenic atoms lie in fourfold inversion axes, the aspect of the tetrahedron is fixed by symmetry. If reasonable assumptions are made concerning its size, it is only necessary to rotate the tetrahedron about the axis, and to find the position which best agrees with the indicative intensities. The As-O distance in the arsenate anion has been reported as 1.73 Å. in YAsO_4 and as 1.66 Å. in BAsO_4 (*Strukturbericht*, 3). A value independent of parameter determinations may be obtained by comparison of the cell volumes of arsenates with respect to isomorphous phosphates of the same cation; for instance, AlPO_4 and AlAsO_4 ; BPO_4 and BAsO_4 . This indicates that the arsenate group is about 3.5% larger than the phosphate group. Since the P-O distance in the phosphate group has been accurately determined as 1.56 Å., the As-O distance in the arsenate ion may safely be taken as 1.63 Å.

From these considerations it has been possible to derive satisfactory parameters for the oxygen, though no high degree of accuracy can be claimed. The results, expressed in fractions of the unit cell, are:

$$x=0.213, \quad y=0.149, \quad z=0.080.$$

Table 1 gives the data for the first half of the powder pattern showing the comparison between visually

estimated intensities and intensity numbers calculated on the basis of the proposed structure. These numbers (which have been reduced by a convenient factor) were obtained from the expression, $I \sim \text{L.P. } pF^2$, where L.P. is the appropriate Lorentz polarization factor, p is the multiplicity and $F^2 = A^2 + B^2$.

Interatomic distances and structure

The O-As distances in the arsenate group have been assumed to be 1.63 Å. For the most reasonable position of this group with reference to the bismuth positions, the bismuth is found to have a co-ordination ring of eight oxygen atoms. Four are at 2.49 Å., four others at 2.59 Å. All other oxygen atoms are more than 4 Å. away. The average oxygen distance to nearest neighbor oxygen atoms is 2.85 Å., the individual distances being 2.60, 2.75, 3.02 and 3.02 Å.

Tetragonal bismuth arsenate has the scheelite structure (CaWO_4). Other crystals which have this structure are the periodates of sodium, potassium, ammonium and rubidium; the perhenates of silver, sodium, ammonium and rubidium; the molybdates of lead, strontium, calcium and barium. No other arsenate is known to have this structure. Bismuth vanadate is reported to have an orthorhombic cell which is of a deformed scheelite type.

This paper is based on work done under the auspices of the Manhattan District at the Metallurgical Laboratory, University of Chicago.

References

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Evaluation of Fourier Transforms by a Fourier Synthesis Method

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A convenient numerical method is developed for evaluating the Fourier transforms of arbitrary functions by the use of Beavers-Lipson strips. A detailed procedure is worked out for the determination of the radial distribution curve of an amorphous material from the X-ray diffraction intensity curve, but the method is generally applicable provided that the transformed function is continuous and approaches zero sufficiently rapidly. For the purpose considered, strips giving values of $A \sin 2\pi nx$ at intervals of $\frac{1}{120}$ in x to two-figure accuracy and extending up to the 45th harmonic are shown to be suitable. The accuracy of the method has been tested by evaluating the transforms of the first three odd Hermite functions with satisfactory results.

Introduction

In the study of amorphous materials by X-ray diffraction the experimental data are obtained in the form

of a curve relating the intensity of diffracted radiation to the Bragg angle of diffraction, θ . This can be converted into a radial distribution function of the electron