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### *The crystal-structure of the bismuth oxyhalides.*

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A. DE SCHULTEN<sup>1</sup> published a crystallographic and optical investigation of the bismuth oxyhalides in 1900. He succeeded in preparing minute square plates capped with pyramidal planes, but evidently the difficulties of manipulation prevented the measurement of interfacial angles. He did, however, record a negative uniaxial figure observed in a direction perpendicular to the plane of the square plates of all three salts BiOCl, BiOBr, and BiOI. The present work was undertaken to extend A. de Schulten's observations, to measure the axial ratios, and to determine the crystal-structure.

It was desirable to obtain single crystals sufficiently large to mount for goniometric and X-ray work. This was finally achieved by a diffusion method. A concentrated solution of bismuth chloride in hydrochloric acid was poured into a small crystallizing dish, and then, disturbing as little as possible the contents of the dish, layers of hydrochloric acid of diminishing concentration were slowly added. The dish was then filled to the top with water and a surrounding larger dish also completely filled with water. The larger dish was then covered with a glass plate and left undisturbed at a constant temperature of about 18° C. for three days. Prolonging the duration of the experiment did not produce larger crystals, but sometimes a

<sup>1</sup> A. de Schulten, Bull. Soc. Chim. Paris, 1900, vol. 23, p. 156.

re-solution or the deposition of polycrystalline spherules on the faces of the single crystals already formed. It was found advisable to drain off the liquid at the end of three days and allow the inner dish to dry. The best crystals were always found on the inside wall of the smaller dish, and a few of these, after several unsuccessful attempts, were withdrawn on very thin glass fibres without any adhesive. The greatest care is necessary during this operation to avoid crushing or bending the very soft minute plates. Owing to their extremely perfect basal cleavage preservation of the single crystals in a medium under a cover glass is almost impossible. The above procedure was successful in producing square plates of both  $\text{BiOCl}$  and  $\text{BiOBr}$  measuring  $0.3 \times 0.3 \times 0.05$  mm. The preparation of single crystals of  $\text{BiOI}$  is more difficult. The formation of the insoluble bismuth iodide  $\text{BI}_3$ , which is not readily hydrolysed, is prevented by dissolving bismuth oxide  $\text{Bi}_2\text{O}_3$  in an excess of hydriodic acid. The compound  $\text{HBI}_4$  is then formed, which is hydrolysed by adding a large excess of water and gradually raising the temperature to boiling-point. Very thin red folia of  $\text{BiOI}$  obtained by this method when examined by X-ray photographs are found to consist of a small number of single crystals superposed almost in parallel position.

*Crystallography.*—The basal reflections from a number of  $\text{BiOCl}$  plates were examined with a pin-point light source. The basal planes not in contact with the glass dish during growth show a light-figure consisting of four V-shaped reflections which, prolonged by straight lines, form a rhombus, not quite a true square. These reflections come from four very flat pyramid faces inclined to the basal plane by  $1^\circ 18\frac{1}{4}'$  and  $1^\circ 29\frac{1}{4}'$  respectively. The indices of these planes referred to the axial ratio  $a:c = 1:1.895$  are approximately (1.1.118) and (1.1.103). Similar measurements of a number of  $\text{BiOBr}$  crystals show flat pyramidal faces inclined at  $4^\circ 23\frac{1}{2}'$  and  $4^\circ 51'$  to the basal plane. These angles correspond to planes (1.1.38) and (1.1.34) respectively, referred to the axial ratio  $a:c = 1:2.068$ . Truly square light-figures were also observed on one crystal reflected from the plane (1.1.84) inclined at  $2^\circ 3'$  to the basal plane. No crystals of  $\text{BiOCl}$  or  $\text{BiOBr}$  prepared by this method showed the planes (111) and the prism faces (110) were always too small to yield reflections. The  $\text{BiOI}$  preparation yielded crystals showing only (001) sometimes with edges parallel to (110). Single crystals of both  $\text{BiOCl}$  and  $\text{BiOBr}$  yield Laue photographs showing true tetragonal symmetry, and the apparently orthorhombic form of the pyramid faces vicinal

to (001) is possibly due to the distorting influence of growth in contact with the cylindrical surface of the crystallizing dish.

*X-ray measurements.*—Rotation photographs of all three salts were obtained about the [110] and [001] axes, the former axis being parallel to an edge of the square plate and the latter, of course, perpendicular to the plane of the plate. The sub-parallel growths of BiOI did not yield photographs so perfect as those of BiOCl and BiOBr, but accurate cell-dimensions were obtained and the relative intensities of the basal diffractions were readily estimated. Slightly mis-set rotation photographs of BiOCl and BiOBr were also used for comparison of the intensities of the basal diffractions. Oscillation photographs show that the space-group is  $P4/nmm = D_{4h}^7$  and the unit cells contain 2 BiOCl, 2 BiOBr, and 2 BiOI respectively.

Table 1 gives the unit-cell dimensions, specific gravities, and the crystal-structure parameters for the bismuth oxyhalides. Data for the isostructural matlockite<sup>1</sup> and PbFBr<sup>2</sup> are added for comparison.

TABLE 1. *X-ray data and specific gravities of the bismuth oxyhalides, &c.*

	Unit-cell dimensions		Calculated axial ratio.	Specific gravity		Crystal-structure parameters	
	<i>a.</i>	<i>c.</i>		Observed.	Calculated.	<i>u.</i>	<i>v.</i>
BiOCl ...	3.89	7.37 Å.	1:1.895	7.717	7.70	0.171	0.650
BiOBr ...	3.92	8.11	1:2.068	8.082	8.07	0.153	0.650
BiOI ...	4.01	9.14	1:2.279	7.922	7.90	0.132	0.667
PbFCl ...	4.09	7.21	1:1.763	7.05	7.16	0.208	0.650
PbFBr ...	4.18	7.59	1:1.816	7.52	7.61	0.195	0.650

Data for PbFCl from the mineral matlockite, F. A. Bannister, 1934.

Sp. gr. of BiOCl, BiOBr, and BiOI, A. de Schulten, 1900.

Sp. gr. of PbFBr, W. Nieuwenkamp and J. M. Bijvoet, 1932.

All possess the matlockite type of crystal-structure. The parameters of the bismuth and halogen atoms in the oxyhalide structures have been evaluated from a comparison of intensities of the basal diffractions (table 2). Intensities of diffraction for all other types of lattice-plane also agree well with the calculated structure-factors. A formal development of the crystal-structure from the space-group and intensity data has previously been given for matlockite.<sup>2</sup> It is unnecessary to repeat the treatment in detail for the bismuth oxyhalides. Their crystal-structures are defined as for matlockite by the atomic positions: Bi,  $00u$ ,  $\frac{1}{2}\frac{1}{2}\bar{u}$ ; X,  $00v$ ,  $\frac{1}{2}\frac{1}{2}\bar{v}$ ; O,  $\frac{1}{2}00$ ,  $0\frac{1}{2}0$ ,

<sup>1</sup> W. Nieuwenkamp and J. M. Bijvoet, Zeits. Krist., 1932, vol. 82, p. 157. [M.A. 5-177.]

<sup>2</sup> F. A. Bannister, Min. Mag., 1934, vol. 23, pp. 587-597.

where Bi takes the place of lead, oxygen of fluorine, and X represents chlorine, bromine, and iodine in turn.

TABLE 2. Comparison of observed intensities (*I*) and calculated structure-factors (*S'*) for rotation photographs of single crystals of *PbFCl*, *BiOCl*, *BiOBr*, and *BiOI*.

Diffracting plane.	<i>PbFCl</i>		<i>BiOCl</i>		<i>BiOBr</i>		<i>BiOI</i>	
	<i>I</i> .	<i>S'</i> .	<i>I</i> .	<i>S'</i> .	<i>I</i> .	<i>S'</i> .	<i>I</i> .	<i>S'</i> .
(001)	m	24.2	s	37.4	s	35.2	s	38.5
(002)	vs	-59.6	s	-37.8	m	-27.9	m	-23.9
(003)	mw	-29.3	vs	-52.0	m	36.0	nil	-6.8
(004)	w	27.4	ms*	-29.7	vs	-65.5	vs	-81.6
(005)	s	58.0	ms	38.1	nil	9.8	ms	-47.9
(006)	vwv	10.0	vs	60.2	vs	66.8	ms	52.3
(007)	m	-49.5	vw	11.0	mw	28.5		
(008)	vw	-17.5	mw	-26.2	vwv	12.1		
(009)	ms	29.0	s	-35.5	w	-21.1		
(0.0.10)	not on film		vwv	-8.9	s	-32.4		

\* (004) coincides with (113) on the rotation photograph of *BiOCl*; both are equally strong on oscillation photographs from which the tabulated intensity of (004) has been estimated.

Cu-K $\alpha$  radiation with nickel filter was used,  $\lambda = 1.539 \text{ \AA}$ .

s = strong, m = medium, w = weak, vw = very weak, &c.

The *S'* values are calculated from the following expressions:

For  $h+k$  even and both  $h$  and  $k$  even:  $S' = \text{Pb} \cos 2\pi ul + \text{Cl} \cos 2\pi vl + \text{F}$ .

For  $h+k$  even and both  $h$  and  $k$  odd:  $S' = \text{Pb} \cos 2\pi ul + \text{Cl} \cos 2\pi vl - \text{F}$ .

For  $h+k$  odd:  $S' = \text{Pb} \sin 2\pi ul + \text{Cl} \sin 2\pi vl$ .

The accuracy of cell-dimensions measured by the rotation photograph method was checked by powder photographs. A small amount of each salt was finely ground and painted on a thin glass fibre, then centred and left stationary in the X-ray beam. Exact agreement in cell-dimensions was obtained by the two methods, but the powder photographs show a general increase in intensity of all the (00*l*) lines and a marked blackening of these lines near the equator. Both facts are due to the minute cleavage flakes of oxyhalide adhering with their cleavage faces parallel to the axis of the glass fibre. A precipitate of *BiOCl* was then prepared by adding a large amount of water to a solution of bismuth chloride. The fine-grained material that remained floating on the water-surface was filtered and dried and a small compact portion mounted at the end of a glass fibre. In this way it was hoped to prevent the orientation produced by the grinding and painting process mentioned above. The intensities of the (00*l*) diffractions on the resulting powder photograph are considerably reduced and only the first three orders are faintly visible. The high

order diffractions ( $hkl$ ) are somewhat diffuse and show that the average grain-size of this specimen of BiOCl is approximately  $10^{-6}$  cm. It is natural to assume that the grains are minute plates and these probably possess an average thickness less than  $10^{-6}$  cm. Thus the ( $00l$ ) lines should be broader, and therefore weaker, than the ( $hkl$ ) lines.

The evaluation of interionic distances for the three oxyhalides of bismuth, matlockite, and lead fluobromide leads to some interesting conclusions (table 3). The distance between the centres of bismuth

TABLE 3. *Interionic distances calculated from the crystal-structures of the bismuth oxyhalides, matlockite, and lead fluobromide.*

	Bi-O.	Bi-X.	$X_v-X_v$ .	$X_v-X_{\bar{v}}$ .	Theoretical diameter of X.
BiOCl... ..	2.32	3.05	3.89	3.53	3.60 Å.
BiOBr... ..	2.32	3.20	3.92	3.69	3.92
BiOI ... ..	2.34	3.38	4.01	4.17	4.40
	Pb-F.	Pb-X.	$X_v-X_v$ .	$X_v-X_{\bar{v}}$ .	Theoretical diameter of X.
PbFCl* ... ..	2.54	3.07	4.09	3.62	3.60 Å.
PbFBr ... ..	2.56	3.18	4.18	3.73	3.92

\* Data for matlockite and the artificial salt.

X represents Cl, Br, or I.

$X_v-X_v$  is the shortest interionic distance in one and the same layer of halogen ions placed at  $00v$ .

$X_v-X_{\bar{v}}$  is the shortest interionic distance between contiguous layers of halogen ions placed at  $00v$  and  $\frac{1}{2}\bar{v}$ .

and oxygen ions can be calculated directly from the values of  $u$  given in table I, and is almost identical for all three oxyhalides. Assuming that the diameter of the oxygen ion  $O^{-2}$  is 1.32 Å., the diameter of the bismuth ion  $Bi^{+3}$  cannot therefore be greater than 1.01 Å. The corresponding distance between the lead and fluorine ions of matlockite and lead fluobromide yields a maximum diameter of 1.22 Å. for the lead ion  $Pb^{+2}$ .

The halogen ions form a double layer  $00v, \frac{1}{2}\bar{v}$  in all five structures. Both for bismuth oxychloride and matlockite the distance between two chlorine ions in one and the same layer and also between contiguous layers is not less than the usually accepted value for the diameter of the univalent chlorine ion, 3.60 Å. The observed interhalogen distance between contiguous layers for the two bromine salts is, however, a good deal less than the diameter of a univalent bromine ion, 3.92 Å. In both these salts, therefore, we obtain evidence that the small positively-charged bismuth or lead atoms are polarizing, i.e. distorting, the large negatively-charged bromine atoms; moreover,

the polarization is more marked along the *c*-axis, i.e. between contiguous layers; than along the *a*-axis. Bismuth oxyiodide is an example of a salt in which the distortion produced by the bismuth kation compresses the double iodine layer in both directions, so that the distance I-I in one and the same layer (4.01 Å.) and between contiguous layers (4.17 Å.) is considerably less than the diameter of an undistorted univalent iodine ion (4.40 Å.). The red colour of the oxyiodide is also an indication of marked polarization.

Crystal-structures of the layer type not infrequently exhibit asymmetric polarization of the anions. The interest of the bismuth oxyhalide structures lies in the progressive polarization observed in passing from the oxychloride to the oxyiodide. The more pronounced the polarization the more pronounced become the 'layer-type properties'. Single crystals of BiOBr possess a more perfect *c*-cleavage than crystals of BiOCl, whilst several attempts to grow crystals of BiOI resulted in folia several millimetres in area but < 0.01 mm. thick.

A large increase in birefringence would also be expected for the oxybromide and oxyiodide. A uniaxial interference-figure with negative sign was observed for all three oxyhalides. Unfortunately, refractive index and birefringence measurements are extremely difficult and, so far as my own trials are concerned, impossible excepting for the oxychloride. The observation of the Becke line when the tiny flakes are pressed into a sulphur-selenium melt becomes uncertain owing to the thinning-out by cleavage. Presumably the shearing produces thinner flakes of the oxybromide and iodide than of the oxychloride. The same difficulty was also encountered in endeavouring to measure the refractive indices of artificial PbFCl precipitated in the form of a powder. It was, however, comparatively simple to observe the Becke line with crushed flakes of the mineral matlockite. The refractive index data obtained are  $\omega$  2.15 for BiOCl, and 2.11 for matlockite (cf. value obtained by the prism method, 2.124),  $\lambda$  approximately 6708 Å.

The difficulty of obtaining reliable optical data on fine-grained material of high-refractive index and birefringence is also encountered when proceeding to distinguish between two very rare minerals, bismoclite and daubreite, both oxychlorides of bismuth. In the circumstances their distinction rests entirely on chemical and X-ray work, and therefore forms a mineralogical application of the above study.

Professor E. D. Mountain recently submitted for X-ray examination the unique specimen of his new mineral bismoclite (this vol., p. 59), which has a chemical composition close to that of bismuth oxychloride. A powder photograph of a small fragment detached from the compact, creamy-white nodule is exactly identical in line positions and intensities with a powder photograph of the artificially prepared salt, and the freedom of the powder lines from flecks shows that the average grain size is  $<10^{-4}$  cm. Both the X-ray and chemical data prove conclusively that the mineral is native bismuth oxychloride. Professor Mountain suggested that the mineral might be closely related to daubreite, a hydrated oxychloride of bismuth described and analysed by Domeyko in 1876.<sup>1</sup>

Bismuth minerals other than bismuthinite, owing to their powdery character, are so liable to be confused with one another that it was essential to secure for comparison one of the specimens of daubreite originally described by Domeyko himself. Professor A. Lacroix kindly loaned to us several specimens labelled daubreite, Cerro de Tazna, Bolivia, from the mineral collection of the Muséum National d'Histoire Naturelle, Paris. Of these only one contains chlorine. The remainder are earthy specimens of kaolinite impregnated with bismuth arsenate. These are probably to be identified with the uncertain mineral taznite, described by Domeyko<sup>2</sup> in 1877 as an arsenio-antimonate of bismuth from the same locality. There is no doubt that these specimens, most of which came from Daubrée's private collection, were sent by Domeyko from Bolivia, but owing to the similarity in appearance of earthy bismuth minerals they were labelled incorrectly.

It is interesting that the one specimen which contains chlorine and bismuth, but no arsenic, was given to Professor Lacroix by Daubrée himself in 1894. This specimen, labelled daubreite, Cerro de Tazna, Bolivia, catalogue no. 94.247, is a pale-yellow compact mineral showing remnants of columnar structure suggesting alteration from bismuthinite. It is admixed with a clay mineral, probably kaolinite, and on account of the small amount of material available and its

<sup>1</sup> I. Domeyko, *Compt. Rend. Acad. Sci. Paris*, 1876, vol. 82, p. 922; *Mineralojía*, 3rd edit., Santiago de Chile, 1879, p. 297. Not to be confused with daubreelite,  $\text{FeCr}_2\text{S}_4$ , a mineral associated with troilite in meteoric irons, and also named after G. A. Daubrée in the same year by J. L. Smith.

<sup>2</sup> I. Domeyko, *Compt. Rend. Acad. Sci. Paris*, 1877, vol. 85, p. 955, *Min.*, 3rd edit., 1879, p. 298. Preliminary qualitative chemical tests and X-ray work suggest that the so-called taznite is impure compact atelestite, basic bismuth arsenate.

obviously impure nature a chemical analysis was not attempted. Powder photographs of picked fragments, free from clay, are almost identical with powder photographs of artificial bismuth oxychloride, and at first the small differences of pattern were thought to be due to orientation (cf. p. 52). Measurement, however, showed that the unit-cell dimensions differ slightly, and further photographs of other samples confirmed this result.

	<i>a.</i>	<i>c.</i>
Artificial BiOCl ... ..	3.89 ± 0.01	7.37 ± 0.02 Å.
Bismoclite, BiOCl ... ..	3.89 ± 0.01	7.37 ± 0.02
Daubreite, BiO(OH,Cl) ... ..	3.85 ± 0.01	7.40 ± 0.02

The difference in cell-dimensions of daubreite and BiOCl is quite sufficient to cause an alteration of pattern which the eye can readily detect. Certain lines which are resolved as doublets in the BiOCl photograph either close up or widen out in the daubreite photograph. The pairs of lines which show this effect to a marked degree are :

	Width of doublet.				
	Bismoclite		Daubreite		
	Observed.	Calculated.	Observed.	Calculated.	
(110) and (102)...	...	0.100	0.100	0.080	0.074 cm.
(211) and (104)...	...	0.104	0.097	not resolved	0.033
(105) and (220)...	...	not resolved	0.020	0.107	0.123

A probable explanation of the different cell-dimensions of the two minerals is to be sought in their chemical composition and therefore in their crystal-structure. Domeyko's original analysis of daubreite corresponds fairly well with the formula BiO(OH,Cl), where the atomic proportions of hydroxyl and chlorine are nearly equal :

	Daubreite.	BiO(OH,Cl).	BiOCl.
Bi <sub>2</sub> O <sub>3</sub> ...	89.60	92.74	89.41
Cl ... ..	7.50	7.06	13.67
H <sub>2</sub> O... ..	3.84	1.79	—
Fe <sub>2</sub> O <sub>3</sub> ...	0.72	—	—
	<hr/> 101.66	<hr/> 101.59	<hr/> 103.08
Less O = Cl	1.69	1.59	3.08
	<hr/> 99.97	<hr/> 100.00	<hr/> 100.00

The possibility of Domeyko's analysis corresponding to a mixture of bismuth ochre and bismuth oxychloride has not been overlooked. Careful examination of long-exposure powder photographs of the specimen loaned by Professor Lacroix fails to reveal any lines which cannot be indexed on the daubreite lattice.



Evidence from quite another direction also shows that the low chlorine figure obtained by Domeyko was not due wholly to impurities. Mr. Hey has obtained precipitates of hydrated bismuth oxychloride by adding a large excess of ammonia to solutions of bismuth chloride. Powder photographs of a preparation containing only 10.25 % chlorine are identical with the daubreeite photographs but not with those of bismuth oxychloride. Although no preparation with as low a content as 7.5 % chlorine has yet been made it is important to note that Mr. Hey's syntheses are further evidence for the existence of compounds of the type  $\text{BiO}(\text{OH}, \text{Cl})$ . It is possible that daubreeite represents the limit of basicity since no convincing proof of the existence of  $\text{BiO}(\text{OH})$  as a mineral nor of its artificial preparation has been offered.

TABLE 4. *Observed intensities and calculated structure-factors for powder photographs of bismoclite and daubreeite.*

Diffract- ing plane.	$\frac{\sin \theta}{\lambda}$		Observed intensity		Structure-factor $S'$	
	Bismo- clite.	Daubree- ite.	Bismo- clite.	Daubree- ite.	Bismo- clite.	Daubree- ite.
(001)	0.068	0.068	m	m	37.4	37.7
(002)	0.136	0.135	w	w	-37.8	-40.0
(110)	0.182	0.184	ms	ms	76.5	73.4
(102)	0.187	0.188	s	s	70.4	65.3
(003)	0.204	0.203	mw	w	-52.0	-54.2
(211)	0.295	0.298	m	s	44.8	48.0
(104)	0.300	0.300	ms		-59.9	-60.4
(212)	0.318	0.320	s	ms	58.2	53.7
(203)	0.328	0.330	m	w	-49.0	-47.6
(005)	0.339	0.338	nil	nil	38.1	43.8
(105)	0.363	0.362	m	w	-35.3	-33.3
(220)	0.364	0.367		w	56.8	64.1
(214)	0.396	0.397	m	m	-52.7	-52.6
(310)	0.407	0.411	m	w	57.3	60.1
(006)	0.407	0.406		w	60.2	53.4
(223)	0.417	0.420	w	vw	-39.6	-42.6

See table 2, p. 52, for intensity symbols, &c.; cf. p. 53, for low intensities of (00l).

It might be expected that intensity data from powder photographs would reveal whether the crystal-structure of daubreeite differs from that of bismoclite in the random replacement of about one-half the chlorine by hydroxyl ions. A slight change in the parameter of the bismuth ion, however, from 0.171 to 0.175 must also be included in the calculation of structure-factors, and the final result is that very

little difference exists between either the observed intensities or calculated structure-factors (table 4). X-ray work, therefore, is not inconsistent with the possible isomorphous replacement of chlorine by hydroxyl ions.

The distinction between bismoclite and daubreëite, owing to the lack of suitable material for a new analysis of daubreëite, is dependent upon the X-ray identification of artificial hydrated bismuth oxychloride, low in chlorine, with daubreëite, the difference in cell-dimensions of the two minerals, and finally upon Domeyko's original analysis.

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