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**CaTaO<sub>3</sub>: un nouveau composé du type pérovskite.** Par M. GASPERIN, *Laboratoire de Minéralogie-Cristallographie de la Faculté des Sciences, Paris, France*

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**Préparation**

En chauffant aux environs de 1700° un mélange équimoléculaire de Ta<sub>2</sub>O<sub>5</sub> et de CaCO<sub>3</sub>, on obtient un produit blanc d'aspect vitreux. Un cliché de rayons X effectué avec ces parties cristallisées donne le diagramme de poudre d'un corps du type pérovskite, dont toutes les raies principales peuvent s'interpréter dans le système cubique simple avec une arête  $a = 3,88 \pm 0,005 \text{ \AA}$ .

La formule de ce corps est donc du type ABO<sub>3</sub>, et les intensités relatives des raies indiquent que l'ion bivalent est ici le calcium, et que le tantale occupe la place de l'ion tétravalent. On peut supposer une réduction de la valence du tantale à haute température comme on l'a déjà fait pour le composé SnTaO<sub>3</sub> précédemment décrit (Gasperin, 1955). On peut aussi supposer une structure lacunaire CaTa<sub>4/5</sub>O<sub>3</sub>. La formule CaTaO<sub>3</sub> semble la plus probable: en effet, la densité calculée pour CaTa<sub>4/5</sub>O<sub>3</sub> avec  $N = 1$  est de 6,58 g.cm.<sup>-3</sup>; pour CaTaO<sub>3</sub> elle est de 7,6 g.cm.<sup>-3</sup>, et la densité mesurée par la méthode hydrostatique, qui donne toujours une valeur par défaut, est un peu supérieure à 7 g.cm.<sup>-3</sup>.

**Dépouillement des diagrammes de poudre**

En plus des raies d'un corps cubique simple de maille  $a = 3,88 \text{ \AA}$ , le diagramme de poudre du CaTaO<sub>3</sub> offre, comme la plupart des composés du type pérovskite, deux particularités: aux grands angles certaines raies sont multiples et groupées autour de la position moyenne de la raie cubique; d'autre part, aux petits angles, on peut voir des raies très faibles de surstructure.

Le dédoublement de la raie 222 semble indiquer que la maille est devenue monoclinique avec un angle  $\beta$  de 90° 32'. Quant aux raies de surstructure, elles ne peuvent s'expliquer qu'en considérant une maille multiple déduite de la première par la transformation:  $A = 3a$ ,  $B = 3a$ ,

$C = 2a$ . Ceci distingue ce composé des autres tantalates et niobates de type pérovskite déjà connus, dans lesquels on rencontre la déformation monoclinique de quelques degrés, mais où la maille multiple s'obtient toujours en multipliant l'arête primitive par 2 ou par 4. Il est malheureusement impossible, d'après les seules données des clichés de poudre de connaître avec certitude la vraie maille du corps considéré, car il se peut que l'on soit en présence de plusieurs phases. Seule l'obtention de cristaux uniques permettrait de préciser ce point, et de connaître les déplacements d'atomes responsables des modifications de la maille cubique.

Un cliché effectué à 500° montre que, à cette température, les raies de surstructure subsistent alors que les dédoublements ont disparu, ce qui prouve que le réseau a acquis une symétrie supérieure à la symétrie monoclinique.

**Propriétés électriques**

Le composé CaTaO<sub>3</sub> n'ayant pas pu, jusqu'à présent, être obtenu en cristaux de dimensions mesurables, une pastille a été fabriquée pour examiner ses propriétés électriques. Le produit finement broyé avec des liants, pressé et chauffé à 1400°, a donné une pastille de densité 6,3 g.cm.<sup>-3</sup>.

À la température ambiante, cette pastille a une constante diélectrique voisine de 70, qui ne varie pas par refroidissement jusque -180°. Par contre, en chauffant jusque 500°, on observe à 360° une brusque variation de la valeur de  $\epsilon$  qui correspond vraisemblablement au changement de structure traduit sur les clichés de rayons X par la suppression des dédoublements de raies.

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**X-ray diffraction data for anhydrous BiCl<sub>3</sub> and BiBr<sub>3</sub>.\*** By G. M. WOLTEN and S. W. MAYER, *The Research Department of Atomics International, A Division of North American Aviation, Inc., Canoga Park, California, U.S.A.*

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**Introduction**

Sokolova, Urazov & Kuznetsov (1954) have reported two patterns for BiCl<sub>3</sub>. They believed the patterns to represent two crystalline modifications, neither of which was cubic. In order to check these data and to investigate the possibility of polymorphism, an X-ray investigation of BiCl<sub>3</sub> was undertaken, both at room temperature and near the melting point. X-ray data for the closely related

compound BiBr<sub>3</sub> were obtained at room temperature, for comparison with the data reported by Urazov & Sokolova (1954a), and also at elevated temperatures.

**Materials**

Anhydrous BiCl<sub>3</sub> was prepared by drying J. T. Baker's Analytical Reagent under flowing HCl gas, followed by fractional distillation, first under HCl and then under argon. The product had a melting point of 232.2 °C. BiBr<sub>3</sub> was prepared in a Pyrex bomb at 280° by the direct combination of the elements. The product melted at 218°.

\* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. X-ray diffraction patterns of BiCl<sub>3</sub> and BiBr<sub>3</sub>

Indices		BiCl <sub>3</sub>			BiBr <sub>3</sub>		
$h^2 + k^2 + l^2$	$hkl$	$d$ , calc. (Å)	$d$ , found (Å)	Intens.	$d$ , calc. (Å)	$d$ , found (Å)	Intens.
1	(100)	8.14	—	extinct	9.23	—	extinct
2	110	5.756	(5.68)	<i>vw</i> , not pos. identified	6.527	6.4	100
3	111	4.700	4.75	100	5.329	5.35	<i>w</i>
4	200	4.070	4.07	18	4.615	4.58	<i>w</i>
5	210	3.640	3.68	18	4.128	4.13	17
6	211	3.323	3.365	33	3.768	3.83	8
8	220	2.878	2.86	33	3.263	3.259	23
9	221, (300)	2.713	2.73	15	3.077	3.08	22
10	310	2.574	2.58	24	2.919	2.92	80
11	311	2.454	2.44	21	2.783	2.79	33
12	222	2.350	2.38	17	2.665	2.68	36
13	320	2.258	2.23	32	2.560	2.58	10
14	321	2.176	2.15	14	2.467	2.54	15
16	400	2.035	2.04	22	2.308	2.35	40
17	322, 410	1.974	1.95	31	2.239	2.26	12
18	330, 411	1.919	1.91	6	2.176	2.153	33
19	331	1.867	1.857	18	2.118	2.124	20
20	420	1.820	1.84	42	2.064	2.074	35
21	421	1.776	1.76	<i>w</i>	2.014	2.005	<i>w</i>
22	332	1.736	1.73	<i>w</i>	1.968	1.976	20
24	422	1.662	1.69	9	1.884	1.947	45
25	430, (500)	1.628	1.62	<i>w</i>	1.846	1.855	6
26	431, 510	1.596	1.60	7	1.810	1.802	6
27	333, 511	1.567	1.57	6	1.776	1.768	8
29	432, 520	1.512	1.51	7	1.714	1.717	7
30	521	1.486	1.47	10	1.685	1.698	6
32	440	1.439	1.45	8	1.632	1.664	<i>w</i>
33	441, 522	1.417	1.41	24	1.607	1.591	<i>w</i>
34	433, 530	1.396	1.395	<i>w</i>	1.583	1.58	<i>w</i>
35	531	1.376	1.37	<i>w</i>	1.560	1.568	28
36	442, 600	1.357	—	not obs.	1.538	—	not obs.
37	610	1.338	1.33	<i>w</i>	1.517	1.523	<i>w</i>
38	532, 611	1.321	1.325	9	1.497	1.490	<i>w</i>
40	620	1.287	1.29	<i>w</i>	1.459	1.458	<i>w</i>
41	443, 540 621	1.271	—	not obs.	1.442	—	not obs.
42	541	1.256	1.25	<i>w</i>	1.424	—	not obs.
43	533	1.241	1.24	<i>w</i>	1.408	—	not obs.
44	622	1.227	1.224	<i>w</i>	1.392	—	not obs.
45	542, 630	1.213	1.216	26	1.376	1.37	<i>w</i>
46	631	1.200	1.205	10	1.361	—	not obs.
48	444	1.175	1.175	5	1.332	1.33	<i>w</i>
49	632, (700)	1.163	1.169	<i>w</i>	1.319	1.32	<i>w</i>
50	543, 550 710	1.151	1.153	<i>w</i>	1.305	—	not obs.
51	551, 711	1.140	1.140	<i>w</i>	1.293	1.29	<i>w</i>
52	640	1.129	1.127	9	1.280	—	not obs.
53	641, 720	1.118	1.117	<i>w</i>	1.268	—	not obs.
54	552, 633 721	1.108	1.106	<i>w</i>	1.256	—	not obs.
56	642	1.088	1.087	13	1.233	1.233	<i>w</i>
57	544, 722	1.078	1.078	<i>w</i>	1.223	1.22	<i>w</i>
58	730	1.069	1.064	6	1.212	1.213	7
59	553, 731	1.060	1.058	<i>w</i>	1.202	1.205	8
61	643, 650	1.042	1.043	<i>w</i>	1.182	1.192	<i>w</i>
62	651, 732	1.034	1.035	<i>w</i>	1.172	1.177	<i>w</i>
64	800	1.018	1.021	<i>w</i>	1.154	1.152	8
65	652, 740 810	1.010	1.014	<i>w</i>	1.145	—	not obs.
66	554, 741 811	1.002	0.9975	6	1.136	—	not obs.
68	644, 820	0.9871	0.986	24(?)	1.119	1.116	<i>w</i>
69	742, 821	0.9800	—	not obs.	1.111	1.108	<i>w</i>
70	653	0.9729	—	not obs.	1.103	—	not obs.
72	660, 822	0.9593	0.965	<i>w</i>	1.088	—	not obs.
73	661, 830	0.9527	—	not obs.	1.080	1.08	<i>w</i>
74	750, 831	0.9463	—	not obs.	1.073	—	not obs.

Table I (cont.)

Indices			BiCl <sub>3</sub>			BiBr <sub>3</sub>		
$h^2+k^2+l^2$	$hkl$		$d$ , calc. (Å)	$d$ , found (Å)	Intens.	$d$ , calc. (Å)	$d$ , found (Å)	Intens.
75	555,	751	0.9399	0.939	<i>w</i>	1.066	—	not obs.
76		662	0.9337	0.938	<i>w</i>	1.059	—	not obs.
77	654,	832	0.9276	0.929	<i>w</i>	1.052	—	not obs.
78		752	0.9217	0.917	17	1.045	—	not obs.
80		840	0.9101	0.9158	<i>w</i>	1.032	—	not obs.
81	663,	841	0.9044	0.9078	3 ( <i>w</i> )	1.026	—	not obs.
	(900)							
82		910	0.8989	0.901	<i>w</i>	1.019	—	not obs.
83	833,	911	0.8935	0.891	6	1.013	—	not obs.
84		842	0.8881	0.885	<i>w</i>	1.007	1.007	<i>w</i>
85	760,	920	0.8829	0.883	<i>w</i>	1.001	—	not obs.
86	655,	761	0.8778	0.875	<i>w</i>	0.9953	0.9925	<i>w</i>
	921							
88		664	0.8677	0.871	<i>w</i>	0.9839	—	not obs.
89	762,	843	0.8628	0.864	<i>w</i>	0.9784	—	not obs.
	850,	922						
90	851,	930	0.8580	0.857	<i>w</i>	0.9729	0.974	<i>w</i>
91		931	0.8533	0.850	<i>w</i>	0.9676	—	not obs.
93		852	0.8441	0.8441	<i>w</i>	0.9571	0.956	<i>w</i>
94		932	0.8396	0.840	<i>w</i>	0.9520	0.9509	<i>w</i>
96		844	0.8308	0.835	<i>w</i>	0.9420	0.943	<i>w</i>
97	665,	940	0.8265	—	not obs.	0.9372	—	not obs.
98	770,	853	0.8223	0.822	<i>w</i>	0.9324	—	not obs.
	941							
99	771,	933	0.8181	0.818	<i>w</i>	0.9276	—	not obs.
100		860, 10,0,0	0.8140	—	not obs.	0.9230	—	not obs.
101	861,	942	0.8100	0.809	<i>w</i>	0.9184	—	not obs.
	10,1,0							
102	772,	10,1,1	0.8060	0.807	<i>w</i>	0.9139	—	not obs.
104	862,	10,2,0	0.7982	0.799	17	0.9051	—	not obs.
105	854,	10,2,1	0.7944	0.793	12	0.9008	0.899	<i>w</i>
106	943,	950	0.7906	0.790	11	0.8965	—	
107		951	0.7869	0.787	<i>w</i> (?)	0.8923	—	
108	666,	10,2,2	0.7833	0.783	<i>w</i>	0.8882	—	
109	863,	10,3,0	0.7797	0.781	<i>w</i>	0.8841	—	
110	952,	10,3,1	0.7761	0.776	<i>w</i>	0.8800	—	

The listed intensities are proportional to the areas under the peaks of X-ray goniometer recordings and have been calculated as percentages of the strongest line in each pattern.

### Experimental

Because of their extremely deliquescent nature, the halides were stored and samples prepared in a dry-box containing an inert atmosphere. Several specimens from each of several preparations of both materials, protected from air by means of various plastic films and tapes, were examined in a recording X-ray diffractometer. A few patterns for both materials were also obtained on film, with the specimens sealed in Lindemann Glass capillaries. In addition, the pattern of BiCl<sub>3</sub> was recorded, both at room temperature and at 220°, by placing a compressed tablet of the material inside an evacuated goniometer furnace, similar to that described by Chiotti (1953). Copper radiation and a nickel filter were used throughout.

### Results

The  $d$  spacings obtained for BiCl<sub>3</sub> had values in the square root ratios typical of the cubic system. Some of the sharpest lines suggested a value of 8.14 Å for the lattice parameter. Using this value, all possible reflections were calculated up to  $h^2+k^2+l^2 = 110$  and compared with those found experimentally. All lines matched and, of the calculated 93 lines, 84 were found. The unit cell of BiCl<sub>3</sub>

is thus primitive cubic, since none of the few absences were systematic, with the possible exception of missing  $h00$ 's with odd values of  $h$ . Such absences would not be observable, since odd reflections from  $h00$  planes, except 100, coincide with reflections from other planes. Despite the large number of patterns that were obtained, a 100 line was never found in either BiCl<sub>3</sub> or in BiBr<sub>3</sub> (which has the same structure, as shown below), whereas every other forward and most of the back reflections were observed. There is thus strong evidence that the absence of the 100 line is systematic. The only space group consistent with this and with the four formula units per unit cell required by the density is  $P2_13$ .

The  $d$  spacings of the two patterns for BiCl<sub>3</sub> reported by Sokolova *et al.* differ from the ones reported below by various amounts up to 2%. In the main, however, their two patterns appear to deviate in opposite directions, so that the average of their two spacings for a given line often agrees surprisingly well with the value obtained in this work. No support was found for their contention that there are two different structures for BiCl<sub>3</sub>. The high-temperature pattern was found to be identical with that obtained at room temperature, and the absence of a transition was confirmed by thermal analysis of pure BiCl<sub>3</sub>.

Fifty-three lines were observed for  $\text{BiBr}_3$ , and the pattern could be interpreted in terms of the same space group as  $\text{BiCl}_3$ . The lattice parameter is 9.23 Å. Agreement with the data of Urazov & Sokolova is rather poor but some correspondence is recognizable.

Thermal analysis revealed  $\text{BiBr}_3$  to undergo a transition at 158°. However, the X-ray pattern failed to reveal a change of structure up to 195 °C. It may be that the transition is the beginning of free rotation of the molecules without a change of crystal symmetry.

Table 1 lists the completely indexed patterns of  $\text{BiCl}_3$  and  $\text{BiBr}_3$ , giving both calculated and observed spacings and observed intensities.

The authors wish to thank Mr A. J. Darnell of this

department for making pure anhydrous  $\text{BiCl}_3$  available for this work and for preparing some of the diffractometer samples.

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### The crystal structure of sodium polymetaarsenite $(\text{NaAsO}_2)_x$ . By J. W. MENARY, *Research Department, African Explosives and Chemical Industries Ltd, P. O. Northrand, Transvaal, S. Africa*

(Received 15 April 1958)

A certain amount of confusion exists in the literature regarding the formulation of alkali metal arsenites. Thus the formulae  $\text{Na}_2\text{HAsO}_3$  and  $\text{NaAsO}_2$  are used synonymously for sodium arsenite. It has been shown in our laboratories that the data on A.S.T.M. cards numbered 1-0905 ( $\text{Na}_2\text{HAsO}_3$ ) and 7-9 ( $\text{NaAsO}_2$ ) are very similar to the powder pattern of a commercial arsenite which analyses as  $\text{As}_2\text{O}_3 \cdot 0.62 \text{Na}_2\text{O}$ . The powder pattern on card No. 2-0373 ( $\text{Na}_2\text{HAsO}_3$ ) is almost identical with that reported in Table 1 which we have obtained for a

metaarsenite is suggested, is the subject of the present note.

Sodium polymetaarsenite may be prepared either by the reaction of stoichiometric amounts of sodium hydroxide and arsenious oxide, or by crystallization of solutions of arsenious oxide in sodium hydroxide in the appropriate region of the ternary phase diagram (Nelson, 1941).

Single crystals of sodium polymetaarsenite were obtained in the form of thin cleavage flakes by crushing a solidified melt. Unit-cell dimensions were obtained from diffractometer measurements on powder and single crystals and from back-reflection photographs of the *Ok*l reflections. The crystals are orthorhombic with unit-cell dimensions ( $\text{Cu } K\alpha_1 \lambda = 1.54050$ ,  $\text{Cu } K\alpha_2 \lambda = 1.54434$  Å)

$$a = 14.314, \quad b = 6.779, \quad c = 5.086 \text{ Å}.$$

These dimensions are considered to be accurate to within  $\pm 0.005$  Å. Assuming eight formula units,  $\text{NaAsO}_2$ , per unit cell, the calculated density is 3.49 g.cm.<sup>-3</sup>. The calculated density is slightly higher than that determined by pycnometer, 3.40 g.cm.<sup>-3</sup> probably because of incomplete displacement of air from the crystals. Only finely divided, highly imperfect crystals were available in sufficient quantity for the determination.

The extinctions observed establish the space group uniquely as *Pbca*. An inclination Weissenberg photograph of an (100) cleavage flake of sodium polymeta-

Table 1. Powder diffraction data for sodium polymetaarsenite

<i>d</i> (Å)	<i>I</i>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>hkl</i>
7.18	18	200	2.036	5	022
4.93	67	210	1.985	19	412, 231
3.58	92	400	1.912	44	430
3.55	54	211	1.824	32	621
3.40	4	020	1.792	20	800, 431
3.17	100	410	1.740	5	602
2.822	45	021	1.731	< 1	810
2.689	66	411	1.694	8	040
2.627	10	221	1.642	4	630
2.547	16	002	1.606	5	041, 213
2.386	16	600	1.582	< 1	820
2.251	5	610	1.530	16	440, 432
2.213	< 1	421	1.513	17	821
2.154	< 1	230	1.496	4	413
2.072	< 1	402	1.465	5	802, 441

pure compound  $\text{NaAsO}_2$ , the formula of which was established by chemical analysis. Schreinemakers & de Baat (1917) and Nelson (1941), who studied the  $\text{Na}_2\text{O}-\text{As}_2\text{O}_3-\text{H}_2\text{O}$  system, have also demonstrated the existence of this compound. All data in the A.S.T.M. X-ray Powder Data File (1957) for sodium arsenite are therefore incorrect. The compound  $\text{NaAsO}_2$ , for which the name sodium poly-

Table 2. Final parameters from Fourier syntheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
As	0.080	0.103	0.250
O <sub>1</sub>	0.127	0.322	0.405
O <sub>2</sub>	0.154	0.568	0.810
Na <sup>+</sup>	0.306	0.102	0.250