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X-Ray Studies on "Sodium Metabismuthate"

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So-called sodium metabismuthate was prepared using the method of Scholder and Stobbe. X-ray powder photographs indicate that its crystal structure is of the ilmenite type. The Bi parameter was determined. The quadratic form for the lines in the powder photographs is given for a commercial sodium metabismuthate.

So-called sodium metabismuthate ($NaBiO_3$.aq) was prepared using the procedure given by Scholder and Stobbe [1]. The samples were dried over H_2SO_4 *in vacuo*. Water contents between 1.6 and 4.0 % by weight were found, corresponding to a ratio of 0.3—0.6 for H_2O/total bismuth in the samples. The ratio Bi^{5+}/Bi_{total} varied between 88 and 96 %. Analysis of one sample (I) gave: $Na^+:Bi^{5+}:Bi_{total}:H_2O = 1.05:0.96:1.00:0.52$. Powder photographs taken in a Guinier focusing camera using Cu-$K\,a$ radiation indicated a rhombohedral unit cell with $a = 6.21$ Å, $\alpha = 53.°2$ and $V = 143$ Å^3. A few, very weak, extra lines showed that the preparation contained minor amounts of impurities, which, however, could not be identified. No shift in the cell dimensions was found for samples of different compositions. The observed density of (I) was 5.8 in fair agreement with the calculated values of 6.38 for 2 $NaBiO_3$ or 6.58 for 2($NaBiO_3$.0.5 H_2O) per unit cell. The cell dimensions and intensities of the lines in the powder photographs are very similar to those of α-$NaSbO_3$, which was found by Schrewelius [2] to be of the ilmenite type with the unit cell dimensions $a = 6.12$ Å, $\alpha = 51.°1$ and $V = 130$ Å^3. The two compounds are evidently isomorphous. For α-$NaSbO_3$, Schrewelius gave the following data:

Space-group: $R\,\bar{3}$ (No. 148)
Atomic positions: 2 Na at 2(*c*): $\pm(x,x,x)$ with $x = 0.342$
2 Sb at 2(*c*): $\pm(x,x,x)$ with $x = 0.156$
6 O at 6(*f*): $\pm(x,y,z;\ z,x,y;\ y,z,x)$

with $x = 0.54$; $y = -0.03$, and $z = 0.26$.

For the present compound it was only possible to determine the Bi parameter which was found to be 0.160 ± 0.005. In view of the facts that sodium metabismuthate has only slightly larger unit cell dimensions than the water-free α-$NaSbO_3$ and that the positions of the heavy atoms of the two com-

Table 1. Part of the powder photographs of $NaBiO_3$. Cu-Ka radiation.

I obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*hkl* rh	*I* obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*hkl* rh
st	210	210	111	vst	977	978	210
vw	227	—	—	w	1 046	1 047	$11\bar{1}$
st	279	279	100	w	1 115	1 117	200
st	348	349	110	m	1 399	1 398	220
st	631	630	211			1 400	322
vw	677	—	—	vw	1 456	—	—
vw	703	—	—	vw	1 491	—	—
vst	767	768	$1\bar{1}0$	st	1 609	1 608	311
vw	781	—	—			1 609	321
		840	221	m	1 811	1 815	$2\bar{1}0$
m	842	841	222			1 885	$21\bar{1}$
				w	1 888	1 893	333

pounds are very nearly the same, the lattice cannot possibly incorporate the water found in the preparation, which must consequently be combined with the impurities observed. Part of the powder photograph of $NaBiO_3$ is given in Table 1. The investigation evidently shows that $NaBiO_3$ is adequately described as a sodium bismuth(V)oxide.

Commercial "$NaBiO_3.2H_2O$" was also studied but found to be different from the above phase. The yellow preparation "$NaBiO_3.2H_2O$" manufactured by Merck gave rather simple powder photographs which could be explained by assuming a hexagonal unit cell with $a = 5.59$ Å, $c = 7.40$ Å, and $V = 201$ Å^3. Samples with brownish or brownish-black colours, manufactured by Schering-Kahlbaum yielded the same pattern and in addition a number of extra lines. No systematic extinctions were found in the powder photographs. It is worth noting that the hexagonal cell has about the same a axis as $NaBiO_3$ (ilmenite type) when the latter is referred to a hexagonal unit cell with $a = 5.56$ Å and $c = 15.9_5$ Å, which might indicate a structural relationship between the two phases. The Merck sample gave the following composition when analysed: $Na^+:Bi^{5+}:Bi_{total}:H_2O = 0.8:0.8:1.0:5$. The water was calculated by difference. The observed density was 5.0. There are probably two formula units per unit cell of the hexagonal phase, the calculated density being, *e. g.*, 5.2 for $2(NaBiO_3.2H_2O)$ and 6.1 for $2(NaBiO_3.5H_2O)$. The present composi-

Table 2. Part of the powder photograph of "$NaBiO_3 . 2H_2O$" manufactured by Schering-Kahlbaum. Cu-Ka radiation. The extra lines have been omitted.

I obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*hkl*	*I* obs	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*hkl*
m	107	109	001	vw	1 009	1 013	200
w	253	254	100	vw	1 121	1 122	201
m	362	362	101	m	1 193	1 192	112
w	432	432	002	vw	1 225	1 229	103
m	686	685	102	vw	1 445	1 451	202
m	758	760	110	m	1 744	1 736	113
m	867	869	111			1 736	104
vw	983	976	003	vw	1 883	1 881	211

tion of this compound can, however, only be found by carrying out a complete structure determination. Part of the powder photograph of "$NaBiO_3.2H_2O$" (Schering-Kahlbaum) is given in Table 2.

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REFERENCES

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2. Schrewelius, N. *Diss.* Stockholm 1943, p. 24.

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