So spiegelt sich die komplexe Struktur des festen amorphen Se in seiner Schmelze deutlich wider, und zwar bis zu hohen Temperaturen. Die obige Einteilung der experimentell erhaltenen Atomverteilungskurven in eine dritte Gruppe ist also strukturmäßig nicht gerechtfertigt. Das Nebeneinander der drei verschiedenen Ordnungszustände (normales Se-Gitter, aufgeweitete Gitterstruktur und $Se_6$-Ringe) in geschmolzenem Se erklärt vielleicht die Tatsache, daß die Züchtung von Se-Einkristallen aus der Schmelze bisher nicht so recht gelungen ist (vgl. HENKELS [29]).

Der Deutschen Forschungsgemeinschaft sei für vielseitige Unterstützung dieser Untersuchungen bestens gedankt.

---

[29] H. W. HENKELS, J. Appl. Phys. **22**, 916 [1951].

---

# Structures of Bismuth Oxides Formed by Heating Bismuth Film in Air

By P. S. AGGARWAL and A. GOSWAMI

National Chemical Laboratory, Poona-8, India

(Z. Naturforschg. **13 a**, 885—887 [1958]; eingegangen am 9. Juni 1958)

Two new forms of bismuth oxide ($a_0$=5.65 Å and 7.02 Å) have been observed during the oxidation of bismuth films. The well-known tetragonal variety ($a_0$=10.93 Å and $c_0$=5.65 Å) seems to be a superstructure form of oxide (I).

Bismuth forms two well-known oxides $Bi_2O_3$ and $Bi_2O_5$, but the trioxide exists in polymorphic forms whilst the structure of the pentoxide is not known. The existence of the suboxide (BiO) has occasionally been reported [1, 2] but its structure has not yet been established. During the oxidation of bismuth films condensed from vapour phase we have, however, observed two new oxides and the results are reported below.

## Experimental

Bismuth was evaporated in vacuo ($\simeq 10^{-2}$ mm Hg) from a nichrome filament onto glass substrates placed about a few cm away. The evaporation was carried out in a glass tube ($\simeq$ 5 cm. dia.) fitted with a rubber stopper through which the filament terminals were introduced and heating was done by a low voltage a. c. supply. The tube was continuously evacuated from the other side by means of a rotary oil pump. The pressure inside the system was measured by a suitable vacuum gauge.

The deposits were then oxidised either in partial vacuo or in air at about 250 – 300 °C and also by passing over a bunsen flame. In the latter case, however, the deposits melted during oxidation. Both the deposits and the oxide coatings were separately examined before and after oxidation in a Finch type of electron diffraction camera with accelarating voltage of 50 – 65 kV.

## Results

Bismuth generally developed a shining black appearance on condensation onto glass substrate. The diffraction patterns (Fig. 1 *) obtained from deposits-films opaque to transmitted light, indicated that the deposit crystals were hexagonal but polycrystalline in nature and developed a preferred orientation such that the $\{01\bar{1}1\}$ planes were parallel to the glass surface. The orientation was also confirmed from (i) the appearance of $01\bar{1}1$ reflection and its high order in the plane of incidence, (ii) the disposition of arcs corresponding to angles between sets of planes given by the relation

$$\text{Cos}\ \Theta = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2}(h_1 k_2 + h_2 k_1) + \frac{3}{4}(a^2/c^2)\, l_1 l_2}{\sqrt{[h_1^2 + k_1^2 + h_1 k_1 + \frac{3}{4}(a^2/c^2)\, l_1^2]\ [h_2^2 + k_2^2 + h_2 k_2 + \frac{3}{4}(a^2/c^2)\, l_2^2]}}$$

where $\Theta$ is the angle between the two sets of planes $h_1 k_1 i_1 l_1$ and $h_2 k_2 i_2 l_2$ of the crystal and (iii) the theoretical pattern drawn by the method of WILMAN [3].

These deposits, on oxidation in air or in low vacuo, changed in colour from black to greenish-yellow. The pattern (Fig. 2) revealed that the rings were due to polycrystalline deposits and the ring radii were in ratio of $\sqrt{3}$: $\sqrt{4}$: $\sqrt{8}$: $\sqrt{11}$ etc. corresponding to all odd or all even indices of the reflections, thus indicating that the oxide films had a f. c. c. structure with the lattice constant = 5.65 Å. It is interesting to note that the intensities of the

---

[1] S. TANTAR, Z. anorg. Chem. **27**, 437 [1901].

[2] F. J. BRISLEE, J. Chem. Soc. **93**, 154 [1908].

* Fig. 1, 2, 3 and 5 see p. 886 a.

[3] H. WILMAN, Acta Cryst. **5**, 782 [1952].

111 reflection is appreciably stronger than those due to 200, 220 and 311 reflections. Further, there are a few faint rings appearing at positions corresponding to $10\bar{1}0$, $10\bar{1}2$ and $10\bar{1}3$ reflections of a hexagonal form of the oxide (Tab. 1) with $a_0 = 4.04$ Å and $c_0 = 6.57$ Å.

| Intensity | Ring radius $r$ (cm) | $d$ Å | *hkl* (cubic indices) | *hkil* (hexagonal indices) |
|---|---|---|---|---|
| vf | 0.745 | 3.478 | — | $10\bar{1}0$ |
| s | 0.789 | 3.283 | 111 | — |
| s | 0.918 | 2.822 | 200 | — |
| m | 1.074 | 2.412 | — | $10\bar{1}2$ |
| s | 1.283 | 2.020 | 220 | — |
| vvf | 1.40 | 1.850 | — | $10\bar{1}3$ |
| s | 1.526 | 1.698 | 311 | — |
| vvf | 1.58 | 1.640 | 222 | — |
| f | 1.680 | 1.538 | — | $20\bar{2}2$ |
| f | 2.035 | 1.276 | 420 | — |
| f | 2.254 | 1.149 | 422 | — |

Table 1. Analysis of the Pattern of Fig. 1.
v=very, s=strong, m=medium, f=faint. $a_0$ (cubic)=5.65 Å; $a_0$ (hexagonal) =4.04 Å; $c_0$ (hexagonal) =6.57 Å.

Bismuth deposits, on oxidation in the bunsen flame, developed a partly green and partly yellowish green colour. The patterns (Fig. 3) show spots as well as rings, but they do not seem to correspond to each other. The spots patterns, on closer examination, appear to be due to two types of single crystal films. The strong network of spots consists of (i) rectangular arrays with the sides in the ratio of $\sqrt{3}: \sqrt{24}$, (ii) 111 reflection and its higher order in the plane of incidence and (iii) spots at 1/3 and 2/3 distance along the diagonal of the rectangle (cf. Fig. 4). This is typical of {111} orientated deposits of f. c. c. crystals when electron beam grazes along $[\bar{1}10]$ and $[110]$ rows of the oxide crystals. This can arise if however the crystals are mutually rotated by 180°. It can also be seen that the faint spots (Fig. 3) are also arranged in a rectangular network of pattern, but with the sides in the ratio $\sqrt{3}: \sqrt{8}$, corresponding to the beam along the $[11\bar{2}]$ rows of the crystals (cf. Fig. 4). These patterns are also repeated after each 30° rotation of the specimen around an axis parallel to the substrate normal. At some places of the specimen the spot pattern due to $\langle 112 \rangle$ direction of the electron beam was more prominent than those due to the $\langle 110 \rangle$ azimuths (Fig. 5). These results show that the oxide consisted of azimuthelly rotated {111} orientated f. c. c. crystal (Fig. 6). The lattice constant (using $11\bar{2}0$ ring of graphite = 1.230 Å as internal standard) was found to be 7.02 Å. The experiment was repeated several times and similar results were obtained.

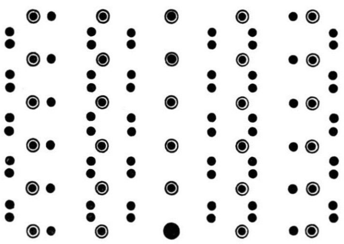

Fig. 4.

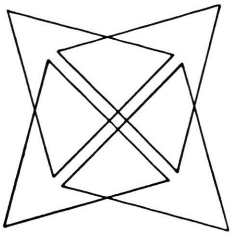

Fig. 6.

It may be noted here that the back ground ring pattern (cf. Figs. 3, 5) was, however, due to bismuth oxide with $a_0 = 5.65$ as obtained during oxidation in air or partial vacuum.

## Discussion

As mentioned before only two oxides of bismuth are well known. The polymorphic trioxide[4] is monoclinic at a low temperature ($a_0 = 5.83$ Å, $b_0 = 8.14$ Å, $c_0 = 13.78$ Å and $\beta \sim 90°$) but tetragonal ($a_0 = 10.93$ Å and $c_0 = 5.62$ Å with 8 molecules in the unit cell) at a higher temperature. Two other cubic phases are often observed on quenching $Bi_2O_3$. The b. c. c. phase ($\gamma$-form, $a_0 = 10.08$ Å) has twelve molecules in the unit cell whereas the sample cubic ($a_0 = 5.52$ Å) has only two.

[4] R. W. G. WYCKOFF, Crystal Structures, Vol. I, Interscience Publishers, New York 1951.

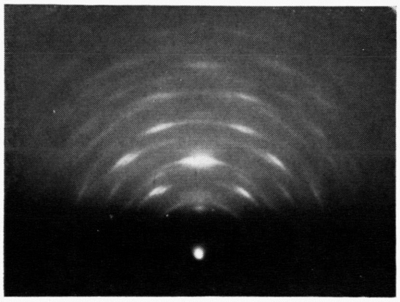

Fig. 1.

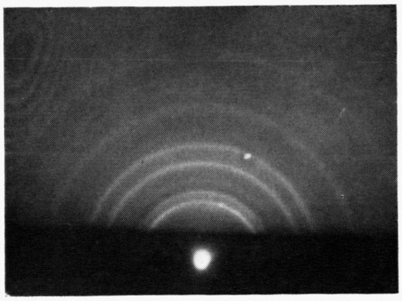

Fig. 2.

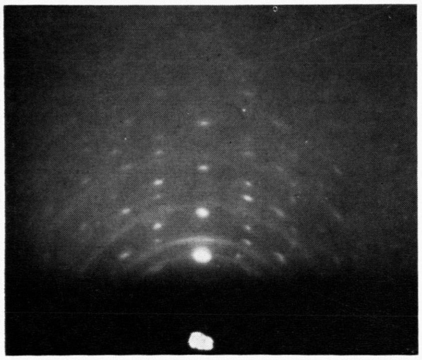

Fig. 3.

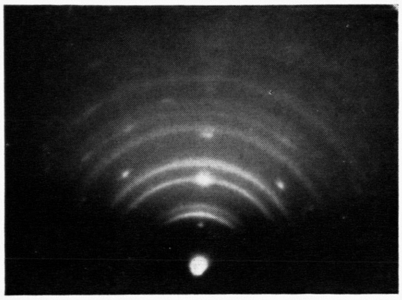

Fig. 4.

The oxides ($a_0 = 5.65$ Å and 7.02 Å hereafter named (I) and (II) respectively) observed by us do not, however, correspond to any of the above oxides. The diffraction patterns (spot or ring type) can not be accounted for by the monoclinic, tetragonal or by the b. c. c. structure. The simple cubic structure which has $a_0$ value closed to the oxide (I) cannot also be confirmed due to the presence of only all odd or even indices of reflections. It is interesting to note that $a_0$ of the tetragonal oxide is nearly twice as much as $c_0$, which is close to the observed value of oxide I. The doubling of $c$ axis along a* of the tetragonal phase may arise as a result of the ordering of atoms of one kind only in the planes (100), (300), (500), etc., and of another kind in (200), (400), etc. thus leading to a superstructure. If, however, these atoms (Bi, O) are equally distributed (statistically) in these planes, the extra reflection due to the special position of the atoms will not appear, hence resulting in the cubic oxide (I) structure. Such superlattice formation are well-known in the case of many binary alloys and also been reported in non metals such as $Cu_2S$ [5] (cubic $a_0 = 5.676$ Å; superlattice tetragonal $a_0 = 5.640$ Å and $c_0 = 11.28$ Å) and FeS [6] (hexagonal $a_0 = 3.43$ Å, $c_0 = 5.694$ Å, superlattice $a_0 = 6.86$ Å and $c_0 = 5.694$ Å).

Bound and Richards [7] and Acharya [8] reported the formation of $Bi_2O_3$ similar to the oxide (I). Semiletov [9] obtained values between 5.5 Å – 5.6 Å by heating $Bi_2Se_3$ and $Bi_2Te_3$ in air and assigned an approximate formula of BiO with NaCl type of structure. The existence of a similar suboxide was also supposed from the magnetic measurement [10] and absorption spectra [11]. It is, however, difficult to ascertain if BiO (AX type of composition) exists in thin films. With the assumption that it does exist, the intense 111 reflection compared to 200, 220 or 311, is not only consistent with the NaCl type of structures as suggested by Semiletov but may also be explained if the atomic positions are

$$A = 000,\ 0\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{1}{2}0\tfrac{1}{2},\ \tfrac{1}{2}\tfrac{1}{2}0; \qquad X = \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4},\ \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4},\ \tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4},\ \tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4}$$

similar to sphalerite.

Since the correlation between the intensity data of electron diffraction pattern and the crystal structure is only approximate unless special precaution is taken in respect of the beam spread and effective thickness of the specimen along the beam direction and also since reflection intensity is often modified as a result of dynamical scattering, it was not possible to determine the position of atoms in the present experimental set up.

The formation of oxide (II) was not reported before. It is, however, difficult to assign the coordinate of the constituents of the crystals even tentatively except that the crystal had a f. c. c. structure, because the intensity of spots is not necessarily directly related to the structure factor [12].

It will be interesting to know why oxide (II) developed single crystal structure whilst the oxide (I) did not during their simultaneous formation. The reasons seem to be that the former has a lower m. p. than the latter and hence during melting and subsequent cooling of the metal, the oxide (II) developed an ordered structure along with the metal underneath whilst the oxide (I) remaining polycrystalline.

Thanks are due to Prof. G. I. Finck for his interest in the work.

---

[5] A. P. B. Sinha, Ph. D. Thesis, London University 1954.

[6] M. R. Piggott and H. Wilman, Acta Cryst. **11**, 93 [1958].

[7] M. Bound and D. A. Richards, Proc. Phys. Soc., Lond. **51**, 256 [1939].

[8] H. K. Acharya, Ph. D. Thesis, London University 1948.

[9] S. A. Semiletov, J. Sci. Industr. Res. **16** A, 377 [1957].

[10] S. S. Bhatnagar, J. Ind. Chem. Soc. **7**, 957 [1930].

[11] N. K. Bridge and H. G. Howell, Proc. Phys. Soc., Lond. A **67**, 44 [1954].

[12] J. M. Cowley, Acta Cryst. **6**, 516 [1953].