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Lattice constants and space groups for several trihalide compounds. By GARY L. BRENNEMAN and ROGER D. WILLETT, *Department of Chemistry, Washington State University, Pullman, Washington 99163, U.S.A.*

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Data are recorded for ammonium tribromide and five quaternary ammonium tribromides and bromochlorides.

In the search for compounds containing trihalide ions suitable for a structure determination preliminary investigations were carried out for several compounds presumed to contain Br_3^- , Br_2Cl^- , or BrCl_2^- ions. These preliminary investigations consisted of growing single crystals, taking rotation photographs and several layers of Weissenberg photographs to determine lattice constants and possible space groups, and measuring the density to obtain the number of molecules per unit cell.

$(\text{CH}_3)_4\text{NBr}_3$, $(\text{CH}_3)_4\text{NBr}_2\text{Cl}$, $(\text{CH}_3)_4\text{NBrCl}_2$, $(\text{C}_2\text{H}_5)_4\text{NBr}_3$, and $(\text{C}_2\text{H}_5)_4\text{NBr}_2\text{Cl}$ were prepared as described by Chattaway & Hoyle (1923). NH_4Br_3 was prepared as described by Roozeboom (1881). The results are shown in Table 1.

References

- CHATTAWAY, F. D. & HOYLE, G. (1923). *J. Chem. Soc.* **123**, 654.
 ROOZEBOOM, H. W. B. (1881). *Ber. deutsch. chem. Ges.* **14**, 2398.

Table 1. *Unit cell data for several trihalide compounds*

Figures in parentheses are standard deviations of several measurements.

Compound	Possible space groups	a	b	c	Molecules per unit cell
$(\text{CH}_3)_4\text{NBr}_3$	<i>Pnnm</i> or <i>Pnn2</i>	13.30 Å (0.01)	9.40 Å (0.01)	23.96 Å (0.01)	12
$(\text{CH}_3)_4\text{NBr}_2\text{Cl}$	<i>Pnnm</i> or <i>Pnn2</i>	13.19 (0.02)	9.36 (0.01)	24.42 (0.01)	12
$(\text{CH}_3)_4\text{NBrCl}_2$	<i>Pnnm</i> or <i>Pnn2</i>	12.41 (0.03)	9.99 (0.02)	23.47 (0.05)	12
$(\text{C}_2\text{H}_5)_4\text{NBr}_3$	<i>Pbcn</i>	27.81 (0.03)	14.19 (0.05)	14.87 (0.04)	16
$(\text{C}_2\text{H}_5)_4\text{NBr}_2\text{Cl}$	<i>Pbcn</i>	27.62 (0.03)	14.08 (0.02)	14.73 (0.03)	16
NH_4Br_3	<i>Pnma</i> or <i>Pn2₁a</i>	9.66 (0.02)	6.27 (0.02)	9.08 (0.02)	4

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The structure of TiO_2 II, a high-pressure phase of TiO_2 . By P. Y. SIMONS* and F. DACHILLE, *Department of Geochemistry and Mineralogy and The Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.*

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TiO_2 II, a high-pressure phase of TiO_2 , is shown to be isostructural with $\alpha\text{-PbO}_2$ from powder X-ray techniques. The structural analysis revealed two sets of Ti-O distances in each octahedron, two at 2.05 ± 0.04 Å and four at 1.91 ± 0.07 Å. A Ti-Ti distance of 3.07 ± 0.04 Å is also observed.

A high-pressure phase of TiO_2 was first prepared by Dacheille & Roy (1962) but the powder pattern was not indexed owing to the small number and poor quality of the diffraction lines, and consequently the structure type was not determined. Jamieson (1965), Simons & Dacheille (1966) and Bendeliany, Popova & Vereshchagin (1966) independently suggested that this phase is isostructural with $\alpha\text{-PbO}_2$. It can easily be prepared from the other titanium dioxide polymorphs: anatase, brookite and rutile (Simons & Dacheille, 1966). Table 1 shows the lattice parameters of the high pressure phase determined by the different investigators as a function of different starting materials. TiO_2 II prepared from anatase was always intergrown with a short

range order phase which produced broad diffraction peaks introducing errors into the 2θ measurements. On the other hand, TiO_2 II synthesized from brookite showed sharp diffraction peaks but the starting brookite crystals were chemically impure with up to ~1% impurity, mostly in the form of iron and silicon. The chemical nature of the rutile boule used by Jamieson and rutile powder used by Bendeliany *et al.* is not known. These factors probably account for the variation in lattice parameters. A paper describing the phase relations of TiO_2 is in preparation.

This structure is not new among high pressure phases, since $\alpha\text{-PbO}_2$ (= PbO_2 II; White, Dacheille & Roy, 1962), MnF_2 II (Azzaria & Dacheille, 1961) and ZnF_2 II (Kabalina & Popova, 1963) also have this structure. Young & Schwartz (1962) found that FeVO_4 (rutile type) transformed to an orthorhombic phase under pressure. The lattice parameters, 2θ values and relative intensities they give indicate

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