Absorption peaks at 2θ angles were recorded on the strip chart and the d values were calculated from the Bragg diffraction law. The results are shown in Table I.

There is excellent agreement in the d values obtained in this study with those previously reported.[7] Likewise, the relative peak intensities match as well as might be expected. No significant difference was found in the results obtained with the pure and the doped sample. The last column of the table shows that no confusion with the rutile pattern is possible. Neither the principal nor the second strongest rutile lines (at d = 3.245 and 1.687 Å., respectively) were found.

On this basis it is concluded that the above samples were both of the anatase structure.

Additional Observations.—An attempt was made to obtain larger single crystals of TiO$_2$ by dissolving the latter in a NaF–KF eutectic melt at high temperatures followed by very slow cooling. The melt was leached in conductivity water; the TiO$_2$ thus obtained was snow-white, but nevertheless contained considerable quantities of the alkali metal and fluoride ions. We were unable to obtain highly purified single crystals. Doped samples containing barium were much whiter than purified TiO$_2$. This shows again that the absence of color is not a suitable criterion of sample purity.

Upon heating the purified TiO$_2$ in air with a Meker burner, no color change was observed, even in the temperature range where a reversible white to yellow transition with commercial samples has been reported.

Heated *in vacuo* at 1000°, the sample sustained a slight irreversible loss of oxygen. This was accompanied by the appearance of a greyish-black cast on the surface of the crystals.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE E. I. DU PONT DE NEMOURS & CO., INC.]

Preparation and X-Ray Study of Niobium Pentaiodide

BY ROBERT F. ROLSTEN

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Crystalline niobium pentaiodide was prepared by reaction of pure niobium and resublimed iodine at 250–285°. X-Ray diffraction data have been obtained.

Introduction

Niobium pentaiodide was first prepared[1] by the reaction between hydrogen iodide and niobium pentabromide. The stable product was not free from bromine and, therefore, was not analyzed. Körösy[2] prepared the pentaiodide by direct reaction of gaseous iodine and an electrically heated (1300–1500°) niobium filament. The red-to-brown colored solid could not be purified. Iodine was not eliminated at 200°, while at 300–400°, the pentaiodide dissociated into a lower iodide and iodine. His observed analytical values of 11.7% Nb, 88.3% I compared to the calculated values of 12.77% Nb, 87.23% I indicate that either niobium was not quantitatively precipitated or the pentaiodide was contaminated with free iodine. Alexander and Fairbrother[3] prepared well-defined, brass-like crystals of pentaiodide by the direct reaction of inductively heated 4–6 mil niobium sheet and excess iodine at 1–2 atmospheres pressure. Repeated attempts were made to analyze these crystals with somewhat inconsistent results arising from the difficulty of separating them quantitatively from traces of metal, lower iodides and from their reactivity on exposure to air. Their results, however, suggest that the crystals were essentially NbI$_5$.

Preparation

The Pyrex glass apparatus contained 1.8 g. of 5 mil acid-cleaned, acetone-dried niobium sheet contained in a 20 mm. tube (14–16 inches long) and resublimed iodine, 10 g. in excess of stoichiometry. The vacuum tight system, with the iodine reservoir cooled in Dry Ice, was heated to 500–550° to outgas the metal and reaction bulb. A system pressure of less than 10^{-6} mm. was maintained for 48 hours. The reaction tube was cooled to room temperature, iodine sublimed from the reservoir was condensed as a solid in the reaction bulb and this bulb was then hermetically sealed. The temperature of the entire bulb was maintained at 265–271°. As the reaction progressed, the active niobium surface was reduced by the condensed, plate-like pentaiodide, which appeared to be black although individual platelets were bronze colored. The unit was slowly cooled to the melting point of I$_2$ (114°) and the excess iodine condensed at one end of the tube which was cooled in an air blast. The iodine removal operation was of 72-hour duration, necessitated by the low temperature level required to prevent disproportionation, or reduction by the residual niobium, of the pentaiodide to lower iodide. The reaction tube was opened in an argon-purged dry box and the lumps of pentaiodide stored in weighing tubes.

Although the above-mentioned preparation is quite satisfactory, it does have the disadvantage that all the available niobium is not transformed to pentaiodide. Therefore, in new experiments, the niobium sheet was supported on a flared and slotted Pyrex tube located in the center of the 20 mm. Pyrex reaction tube. The reaction was again carried out at 280–290° under a partial pressure of iodine to stabilize the temperature sensitive pentaiodide. The large bronze colored crystals were then collected in a very compact form at the bottom of the tube. The unit was opened in a dry box and the pentaiodide stored in weighing bottles. Niobium was determined as Nb$_2$O$_5$ by dissolving the sample in freshly filtered NH$_4$OH, evaporating to dryness, and heating in air in a platinum crucible. Iodine was determined by the modified Volhard[4] technique.

Anal. Calcd. for NbI$_5$: Nb, 12.77; I, 87.23. Found: Nb, 12.81, 12.70, 13.1, 12.70; I, 87.33, 87.55, 87.52, 87.24, 87.17.

X-Ray Study.—The solid pentaiodide was pulverized in an agate mortar cooled by Dry Ice inside an argon-purged dry box. The CO$_2$ provided both a protective atmosphere and permitted the crystalline NbI$_5$ to be pulverized easily. Samples hermetically sealed in 0.2 mm. Lindemann glass

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(1) W. M. Barr, THIS JOURNAL, **30**, 1668 (1908).

(2) F. Körösy, *ibid.*, **61**, 834 (1939).

(3) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, 2472 (1949).

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capillary tubes were mounted in a 114.6 mm. camera and exposed 24 hours to the K-alpha (λ 1.5418 Å.) radiation of copper with an open port and two nickel screens over the film. Samples of different preparations gave identical powder patterns regardless of the capillary size. Lindemann capillaries of 0.5 mm. permitted sample absorption which resulted in line splitting. The observed *d*-spacings (Å.) and visually observed intensities are: 6.09(Broad)(VF); 5.57(Broad)(VF); 3.47(M); 3.24(S); 3.07(M); 3.04(M); 2.40(M); 2.36(M); 2.02(M); 1.86(M); 1.83(M); 1.73(M); 1.70(M); 1.67(M), 1.63(M); 1.53(VF); 1.48(VF); 1.37(M); 1.35(F); 1.29(M); 1.28(M); 1.27(M); 1.25(M); 1.23(F); 1.22(F); 1.181(VF); 1.160(VF); 1.137(VF); 1.122(VF); 1.086(VF).

Discussion

Niobium pentaiodide can be prepared at a lower temperature than reported in the literature. The pentaiodide begins to form from the elements at about 250° and forms rapidly at about 280°. It can be prevented from disproportionating, or being reduced by niobium to lower iodide, by maintaining a partial pressure of iodine. The niobium completely reacted (and thus eliminated contamination from elemental niobium) to form NbI_5 which was collected as a compact crystalline mass of low surface area. The excess iodine was easily sublimed away since the pentaiodide is stable and apparently exerts a very low vapor pressure at the melting point of iodine.

The X-ray diffraction patterns from the different preparations were identical. Single crystals of NbI_5 have not been prepared, and, consequently, there are no data from which reliable lattice parameters can be determined. Therefore, only the observed *d*-spacings are reported.

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WILMINGTON 98, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

Some Ternary Oxides of Tetravalent Molybdenum[1,2]

BY WILLIAM H. MCCARROLL, LEWIS KATZ AND ROLAND WARD

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New oxides of tetravalent molybdenum, having formulas of the type $A_2^{II}Mo_3^{IV}O_8$, have been prepared. The divalent cations which have been used successfully are those of Mg, Mn, Fe, Co, Ni, Zn and Cd. The structure of these compounds has been determined revealing molybdenum to molybdenum bonding and two different coördination numbers for the A cations. Electrical and magnetic properties were examined. Attempts to prepare similar compounds with tetravalent tungsten and rhenium were unsuccessful.

The reported methods for the preparation of molybdenum bronzes analogous to the tungsten bronzes have been examined by Straumanis and Irani[3] who demonstrated that none of the procedures gave a homogeneous product, the only reduced product being MoO_2. These attempts to prepare molybdenum bronzes were all based on the premise that the formal oxidation state of molybdenum would lie between 5 and 6 and that the phases would have a composition M_xMoO_3 where M is an alkali metal and x has a value between zero and one. No ternary oxides of tetravalent molybdenum were known until Scholder, Klemm and Brixner[4,5] reported the preparation of the compounds $BaMoO_3$, $SrMoO_3$, $CaMoO_3$ and $MgMoO_3$. Confirmation of some of these results has been indicated in a recent communication from this Laboratory.[6] However, we were unable to prepare a compound of composition $MgMoO_3$. It was found that by heating molybdenum(IV) oxide with zinc oxide or magnesium oxide, isotypic phases were formed. Chemical analysis of the purified compounds indicated the composition $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$. Part of this paper describes the crystal structure determination of these compounds and the preparation and characterization of other compounds having this structure. In the Discussion, some crystallographic data for $CaMoO_3$ are presented also.

Experimental

Preparation of Reactants.—Molybdenum(IV) oxide was prepared by the reduction of reagent grade molybdenum(VI) oxide with hydrogen at 470° for 36 hours. The product was washed successively with 6 *N* hydrochloric acid, distilled water and 6 *N* ammonium hydroxide until the wash solution was colorless. It was then dried at 110°. Analysis gave 75.05% Mo (theor. 74.99). CoO, NiO and MgO were prepared by heating the carbonates in air at 1000 to 1100° while MnO was obtained by the reduction of MnO_2 at 900° with hydrogen for 36 hours. The other reactants were of C.P. or reagent grade.

Preparation of $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$.—The synthesis of $MgMoO_3$ was attempted by heating in evacuated silica capsules intimate mixtures of reactants according to eq. 1 and 2

$$3MgO + Mo + 2MoO_3 \longrightarrow 3MgMoO_3 \quad (1)$$

$$MgO + MoO_2 \longrightarrow MgMoO_3 \quad (2)$$

The samples were heated for 48 hour periods at 600, 700, 800, 1000, 1100 and 1150°. The brown product obtained at 600° gave an X-ray diffraction pattern of only magnesium oxide and molybdenum(IV) oxide while those formed between 700 and 1000° gave in addition, the pattern of a new phase. At the higher temperatures, products were obtained which gave the pattern of the new phase with only the strongest line of magnesium oxide present. By washing these products with hydrochloric acid, homogeneous black phases were obtained which showed none of the lines of the starting materials in their X-ray patterns. The pattern was indexed on the basis of a hexagonal unit cell. Completely analogous reactions were found using zinc oxide instead of magnesium oxide. The lattice constants and densities are given in Table I (calculated densities in parenthe-

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[1] Abstracted in part from the doctoral thesis of William H. McCarroll submitted to the Graduate School of the University of Connecticut, October, 1956.

[2] This work carried out under contract with the Office of Naval Research. Reproduction in whole or part is permitted for any purpose of the United States Government.

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