and its molybdenum and tungsten analogs are entirely different, apparently due to the reluctance for the 3d-transition metal chromium, unlike the 4d- and 5d-transition metals molybdenum and tungsten, to attain a coordination number greater than six, at least with monodentate ligands.

Acknowledgment.—The author is indebted to Mr. M. B. Bisnette for experimental assistance.

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
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High Temperature, High Pressure Synthesis of a New Bismuth Sulfide

BY M. S. SILVERMAN

Received December 18, 1963

The preparation of a new bismuth sulfide of empirical formula BiS_2 has recently been carried out in our laboratory. To our knowledge, this is the first bismuth sulfide reported with a S:Bi ratio greater than 3:2. The product, consisting of soft, gray, needle-like crystals, resulted when a 4:11 atomic mixture of Bi and S, each of greater than 99% purity, was subjected to a pressure of 50 kbars and a temperature of 1250° for 5–10 min. The tetrahedral anvil apparatus[1] and procedure[2] have been described previously in detail. The only addition was a boron nitride insulating sleeve placed between the sample pellet and the graphite heating sleeve. Excess sulfur present in the product was removed by several CS_2 washings followed by ethanol rinsing and vacuum drying.

Anal. Calcd. for BiS_2: Bi, 76.5; S, 23.5. Found: Bi, 74.0, 73.4; S, 23.0, 23.2. These results were supported by determination of weight losses on oxidation of two samples in pure O_2. Loss calculated for BiS_2 converted to Bi_2O_3: 14.7; found: 14.7, 15.0. The results of analysis of the residue were as follows. *Anal.* Calcd. for Bi_2O_3: Bi, 89.7; S, 0.0. Found: Bi, 90.0; S, <0.1. When heated *in vacuo* to 300°, the product decomposed to Bi_2S_3, as evidenced by the X-ray diffraction pattern of the residue.

The *d* spacings (Å.) and relative intensities of the strongest lines of the X-ray diffraction powder pattern obtained from the new sulfide were: 3.11, 100; 2.91, 60; 2.62, 65; 2.27, 60; 1.88, 70; 1.81, 70; and 1.504, 60.

No conclusions can as yet be drawn about the structure of this sulfide. Nevertheless, the possibility exists that bismuth is present in both +3 and +5 oxidation states, as, *e.g.*, if the compound were Bi^{+3}-$(BiS_4)^{-3}$. We hope to carry out single crystal X-ray studies to determine the structure of the compound.

Acknowledgments.—This investigation was supported in part by the Office of Naval Research. The author is indebted to Dr. J. R. Soulen for helpful discussions and to our analytical and shop groups for their assistance.

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The System Beryllium Oxide–Water at Moderate Temperatures and Pressures[1]

BY HERBERT W. NEWKIRK

Received October 7, 1963

The successful synthesis of BeO crystals by hydrothermal techniques and the design of nuclear reactor components containing BeO for higher ambient service temperatures and pressures requires some knowledge of compound stability regions. This paper reports, in the absence of suitable data,[1–9] the phase relationships which exist at moderate temperatures and pressures in the system $BeO–H_2O$.

Experimental

The impurities in the β-$Be(OH)_2$ powder used in the studies, determined by emission spectrographic analysis, were: Cr, 25 p.p.m.; Cu, 60 p.p.m.; Sn, 12 p.p.m.; Pt, 20 p.p.m.; Si, 60 p.p.m.; Ni, 60 p.p.m.; Al, 12 p.p.m.; Fe, 20 p.p.m.; Mg, 5 p.p.m.; Mn, 7 p.p.m.; Zr, 100 p.p.m.; B, 4 p.p.m.; S, 16,000 p.p.m.

The loss in weight on igniting the β-$Be(OH)_2$ at 1200° was 43.78% and probably represents losses due to the volatilization of water (41.87% theoretical) and the decomposition of anion impurities such as fluorides, sulfates, phosphates, or carbonates. The surface area, measured by nitrogen absorption, was determined to be 45 m.^{2}/g. Observations using the petrographic and electron microscope showed the material to consist mainly of spherical aggregates 0.5–1.0 μ in diameter. Some bladed crystals, 14–23 μ in length, were occasionally observed. The refractive index of these crystals was 1.585 ± 0.015. The optical sign was uniaxial negative and the birefringence was low.

Studies were conducted by wrapping samples of the β-$Be(OH)_2$ powder in platinum envelopes and inserting the envelopes in pressure vessels. The vessels were connected to calibrated Bourdon tube gages and a source of high pressure water by a system of valves and fittings. The vessels were heated at the chosen

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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