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.

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CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
RESEARCH AND DEVELOPMENT DEPARTMENT,
KING OF PRUSSIA, PENNSYLVANIA

High Temperature, High Pressure Synthesis of a New Bismuth Sulfide

BY M. S. SILVERMAN

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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.

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CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
LAWRENCE RADIATION LABORATORY, LIVERMORE, CALIFORNIA

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

BY HERBERT W. NEWKIRK

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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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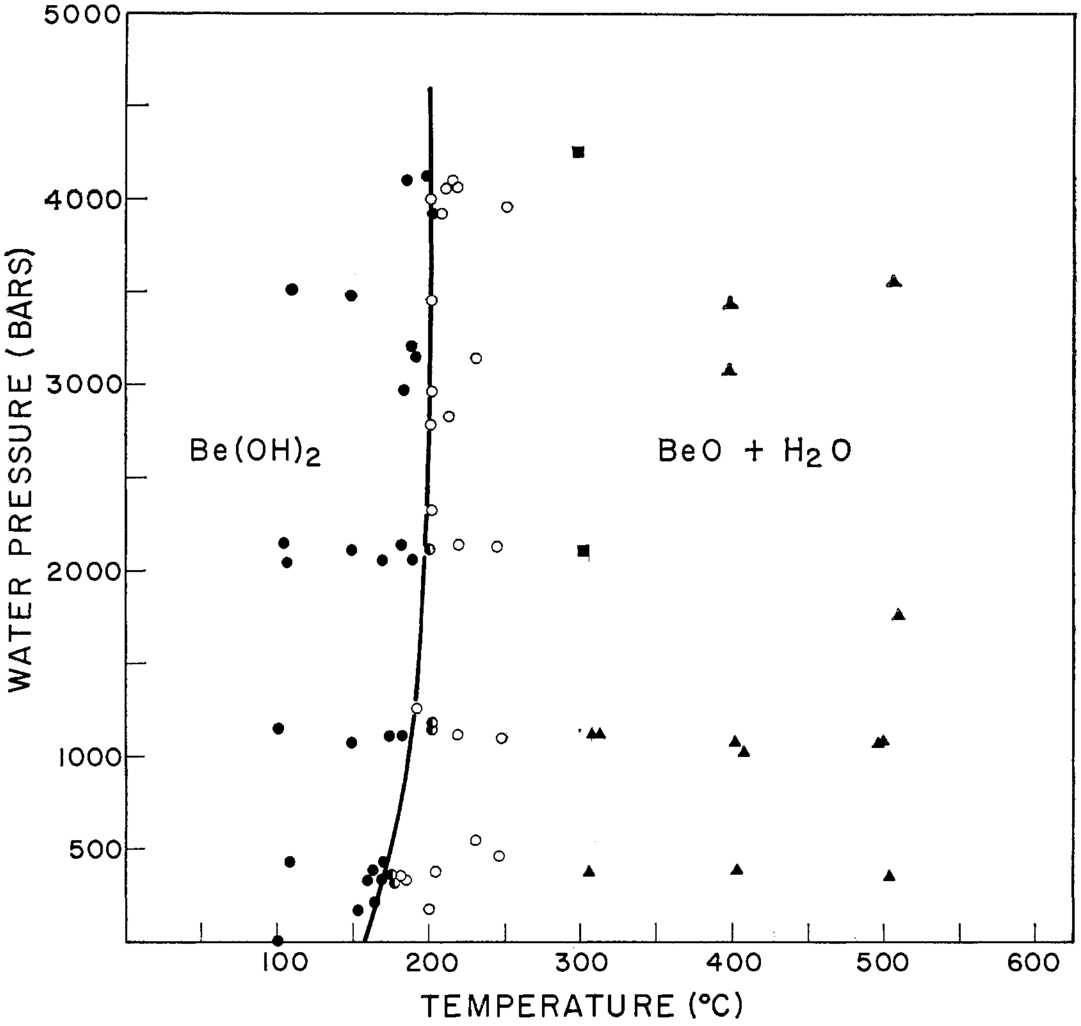

Fig. 1.—Phase relationships in the system $BeO-H_2O$ using β-$Be(OH)_2$ as the starting material: filled circles, β-$Be(OH)_2$; squares, BeO; triangles, well-crystallized BeO; open circles, BeO with enlarged unit cell; half-filled circles, BeO with enlarged unit cell and β-$Be(OH)_2$.

temperature and pressure by nichrome-wound tube furnaces. The vessels could be controlled independently with respect to temperature and pressure. Temperatures were automatically regulated and measured using calibrated chromel–alumel thermocouples inserted in the thermowells of the vessel. At the conclusion of a run, the sample was quenched by venting the vessels to the atmosphere and either rapidly immersing the vessel in cold water or cooling in a blast of air. Temperatures are believed reliable to ±3° and pressures to 3%. The products were examined mainly by X-ray powder diffraction techniques and occasionally with the aid of a petrographic and electron microscope.

Results and Discussion

The results from over 100 hydrothermal experiments are summarized in Fig. 1. Essentially identical results were obtained using powder from a different source and having a different impurity content and morphology. At 4100 bars the maximum temperature at which the hydroxide is stable is 200°; at 300 bars the maximum temperature is 170°. Studies in 2 *N* NaOH and 2 *N* Na_2CO_3 solutions showed identical results.

The BeO formed by dehydration above 300° is always well crystallized. This product typically contains bladed particles 5 μ in length having a refractive index of 1.720. Conversely, BeO formed in the range 175–250° is not well developed and in most cases posseses a larger unit cell than is normally attributed to BeO.[10] In a typical case, the enlargement amounts to a difference of 0.017 Å. along the *c*-axis and 0.013 Å. along the *a*-axis. This material consists mostly of tabular crystals 2 μ in length having a refractive index of 1.628 ± 0.004. Birefringence is moderate to low. The infrared absorption spectra of samples with enlarged unit cells, Fig. 2, show the presence of stretching vibrations of proton and oxygen from water molecules hydrogen bonded to each other and to Be–OH groups at 3500 cm.$^{-1}$. These results support the suspicion that the enlargement of the unit cell is due to the presence of residual water in the crystal lattice. This result was not altogether unexpected since residual moisture has been a continuing problem during infrared analysis of BeO samples[11] and may be responsible for the stress corrosion of polycrystalline bodies.[12]

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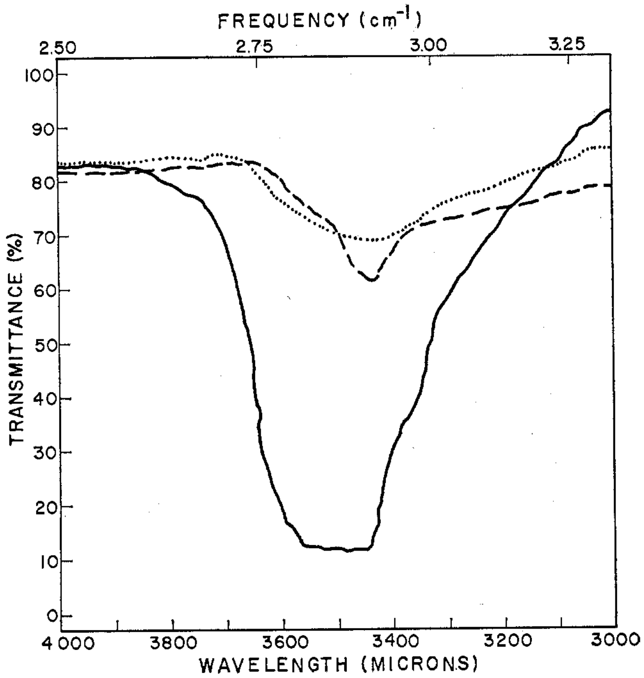

Fig. 2.—The infrared absorption spectra of (a) β-Be(OH)$_2$ (solid line), (b) BeO with enlarged unit cell (dashed line), and (c) well-crystallized BeO formed by dehydration of β-Be(OH)$_2$ during a hydrothermal experiment (dotted line). The presence of the O–H stretching band at 3500 cm.$^{-1}$ suggests that the enlargement of the unit cell in (b) is due to residual water in the crystal lattice.

Samples dehydrated within ±10° of the univariant curve invariably were mixtures of the hydroxide and oxide.

While the conversion of hydroxide to oxide was carried out reproducibly, hydration of the oxide was not realized in these experiments. In other words, BeO is capable of persisting as a metastable phase below its reaction temperature for reasons not well understood at the present time. This difficulty in obtaining equilibrium is not unique to this system and seems to be quite common in oxide–water systems.[13-18] Consequently, the univariant curve as drawn probably does not represent the boundary along which hydroxide, oxide, and water coexist in equilibrium. Therefore, no attempt was made to calculate thermodynamic values, such as heats of reaction, from these data.

Conclusions

It is concluded that the stability region of the BeO phase is well within the capabilities of currently available pressure equipment. Differences in particle size, surface area, and impurity content among starting materials have little effect on the phase relationships in this system. These results confirm the feasibility of growing BeO by hydrothermal techniques; a task recently accomplished for the first time in our laboratory.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF TENNESSEE, KNOXVILLE, TENNESSEE;
ELECTROCHEMICALS DEPARTMENT, E. I. DU PONT DE
NEMOURS AND COMPANY, NIAGARA FALLS, NEW YORK;
AND THE OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE

Potassium Dihydrogen Peroxophosphate: Preparation and Characterization[1a]

BY GLEB MAMANTOV,[1b] JOHN H. BURNS,[1c]
JOSEPH R. HALL,[1b] AND DONALD B. LAKE[1d]

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Peroxophosphoric acid, H_3PO_5, is the phosphorus analog of the better known peroxosulfuric (Caro's) acid, H_2SO_5. Peroxophosphoric acid was prepared for the first time in 1910 by Schmidlin and Massini[2] by carefully bringing into contact concentrated H_2O_2 (usually 30%) with P_2O_5. The direct addition of concentrated H_2O_2 to P_2O_5 results in an extremely exothermic reaction, and some decomposition of the product was impossible to avoid. Schmidlin and Massini found that the H_3PO_5 prepared was quite unstable; only dilute aqueous solutions of H_3PO_5 could be preserved for any length of time. They attempted to prepare salts: in acid solutions no precipitates were obtained upon addition of silver, iron, nickel, manganese, and other heavy metal salts; in neutral solutions, precipitates were obtained which rapidly evolved oxygen and decomposed into phosphates.

In 1937 Toennies[3] tried to moderate the reaction between concentrated H_2O_2 and P_2O_5 by using acetonitrile as an "inert diluent." He claimed to have prepared solutions containing 56–57% of peracid and 19–20% H_2O_2 which were "relatively stable"—after 3 days at -11° $\backsim$51% peracid was present. No preparation of the salts was attempted. We repeated Toennies' preparation and obtained very low yields of H_3PO_5; apparently acetonitrile is hydrolyzed to acetic acid by H_3PO_5.

[1] (a) Presented at the Southeastern Regional Meeting of the American Chemical Society, Nov. 14–16, 1963. (b) Department of Chemistry, University of Tennessee. (c) Oak Ridge National Laboratory. (d) Electrochemicals Department, E. I. du Pont de Nemours and Company.
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