[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Dimorphic Modifications of Beryllium Diiodide, BeI_2[1]

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Two polymorphic modifications of beryllium diiodide have been found. Form I apparently corresponds to the previously described phase, and form II is a heretofore undescribed high-temperature phase stable above 350°. Form I is tetragonal. Powder X-ray diffraction data indicate cell dimensions $a_0 = 6.12 \pm 0.01$ Å., $c_0 = 10.63 \pm 0.02$ Å., $Z = 4$. Form II is orthorhombic with cell dimensions $a_0 = 16.48 \pm 0.02$ Å., $b_0 = 16.702 \pm <0.01$ Å., $c_0 = 11.629 \pm <0.01$ Å., $Z = 32$. Volume per formular unit and Lorentz–Lorenz refraction, respectively, of the two forms are nearly identical.

Introduction

In view of recent work on the subhalides of other elements, particularly aluminum iodide,[2] attempts were made to prepare sub- and superiodides of beryllium. The attempts were unsuccessful, but in the course of this work two polymorphic modifications of beryllium diiodide were found, hereafter designated form I and form II. It seems likely that the previously reported beryllium diiodide[3] corresponds to form I, and that form II is a previously unrecognized high-temperature modification. Because beryllium diiodide is extremely hygroscopic all operations were carried out in sealed glass tubes or in an inert-atmosphere box.

Beryllium Diiodide Form I

Preparation.—Beryllium diiodide form I was prepared by heating beryllium metal chips or diberyllium carbide in a stream of hydrogen and iodine, after the method of Messerknecht and Biltz.[3] Slight modifications permitted use of high-vacuum techniques. Reaction was carried out in silica-glass tubes at various temperatures between 750 and 1100°, and in this range temperature did not appear to affect yield. The products were sealed off in evacuated bulbs fitted with small side arms. On heating the bulbs to about 85° small amounts of silicon tetraiodide impurity (identified by melting point and spectral analysis) sublimed into the side arms which were then sealed off and discarded. The contents of several bulbs were combined and sublimed under vacuum. This product gave a positive test for iodide and gave on analysis 3.39% by weight beryllium, to be compared with 3.43% calculated for BeI_2. No optical or X-ray evidence of inhomogeneity of the product was observed.

Properties.—Most preparations examined consisted of colorless, anhedral grains without pronounced cleavage. One preparation, however, contained some euhedral crystals which were tetragonal dipyramids {112} with basal pinacoid {001} and prism {100}. Lack of suitable material made it impossible to obtain single-crystal X-ray data. The powder X-ray diffraction pattern (Table I) was indexed in terms of a primitive tetragonal cell with dimensions $a_0 = 6.12 \pm 0.01$ Å., $c_0 = 10.63 \pm 0.02$ Å., $c/a = 1.73_7$. All observed diffraction lines of type $0kl$ had k even and $(h + k)$ was even for all lines of type $hk0$, suggesting space group P4/nbm (D^3_{4h}) in which the number of formular units per cell must be an integral multiple of two. Assuming four formular units per cell gives a volume per formular unit of $99._5$ Å.^{3} and a calculated density (formula weight 262.85; weight of unit atomic weight 1.6602×10^{-24} g.) of 4.38 g. per cc. For beryllium diiodide prepared in like manner and purified by sublimation, and therefore probably corresponding to form I of the present paper, Messerknecht and Biltz[3] reported a measured density of 4.325 g. per cc.

The crystals were optically uniaxial positive with very low birefringence and refractive indices for the ordinary and extraordinary rays near 1.99. The Lorentz–Lorenz refraction is $29._8$ cc.

Although samples for powder X-ray diffraction were prepared in an inert-atmosphere box with dew point below −60°, this form of beryllium diiodide exhibited a tendency to decompose on grinding in a mortar. Extreme care had to be exercised to avoid such decomposition which was evidenced by development of brown color in streaks corresponding to the more vigorous strokes of the pestle. No such tendency to decompose on grinding was observed with form II described below.

Beryllium Diiodide Form II

Preparation.—Beryllium diiodide form I and beryllium metal chips were sealed in borosilicate-glass tubes and heated for various lengths of time at various temperatures. When heated above 350° for a few hours form I was converted to form II. Attempts to separate form II from the metal chips by sublimation proved unsuccessful; when heated to about 450° form II sublimed, form I appearing as the condensation product. Although this might appear to indicate that form I is the high-temperature modification, the temperature at which crystal growth took place on condensation was believed to be well below 350°, the approximate temperature at which form I changed to form II on heating. Therefore form II is regarded as the high-temperature polymorph.

Beryllium diiodide form I and iodine sealed in borosilicate-glass tubes and heated to about 300° overnight gave form II and iodine. Most of the excess iodine was removed on heating this product under vacuum at about 150°. Analysis of the material thus purified gave 3.60% by weight beryllium. If the remainder is assumed to be iodine this corresponds to an iodine-to-beryllium ratio of 1.9. The fact that the same crystal species resulted from heating beryllium diiodide form I with excess beryllium and with excess iodine makes it highly improbable that this deviation from the stoichiometric ratio of 2 is significant; it is believed attributable to difficulty in analyzing such extremely hygroscopic materials. As will be shown, the two beryllium iodides have nearly identical molecular volumes and Lorentz–Lorenz refractions, this lending further support to the contention that they do not differ in composition.

Properties.—Calibrated Weissenberg and precession photographs indicate, with the exception of two faint reflections, diffraction symbol mmmB-ab, otherwise diffraction symbol mmmP-an, and give cell dimensions $a_0 = 16.48 \pm 0.02$ Å., $b_0 = 16.702 \pm <0.01$ Å., $c_0 = 11.629 \pm <0.01$ Å.; volume per formular unit 100 Å.^{3}; $a{:}b{:}c = 0.987{:}1{:}0.696$. The density calculated assuming 32 formular units per cell is 4.36 g. per cc.

The crystals exhibit prominent cleavage parallel to {010} and less prominent cleavage parallel to {001}. They are colorless and optically biaxial positive with optic axial angle 25° for sodium light and very weak dispersion $r < v$. The principal refractive indices for sodium light are 1.952 ± 0.005, 1.954 ± 0.005, 1.988 ± 0.005; geometric mean 1.965; Lorentz–Lorenz refraction 29.4 cc. The optic orientation is $X = c$, $Y = b$, $Z = a$.

Structural Considerations.—All prominent X-ray diffraction spots appearing in single-crystal photographs, and all the diffraction lines appearing in the powder pattern (Table II), have indices satisfying the conditions $h = 4n$, $k = 4n$, $h/4 + k/4 + l/2 = 2n$. This indicates a monomolecular orthorhombic pseudocell with dimensions $a_0' = 4.120$, $b_0' = 4.176$, $c_0' = 5.815$ Å. (obtained from the true cell by the transformation 1/4, 0, 0/0, 1/4, 0/0, 0, 1/2) with an

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] J. D. Corbett and S. von Winbush, THIS JOURNAL, **77**, 3964 (1955).

[3] C. Messerknecht and W. Biltz, *Z. anorg. allgem. Chem.*, **148**, 152 (1925).

TABLE I

PARTIAL POWDER X-RAY DIFFRACTION PATTERN OF BERYLLIUM DIIODIDE, FORM I

hkl	*d*, Å.		I/I_1[b]
	Calcd.	Obsd.[a]	
110	4.33	4.31	10
112	3.36	3.33	100
200	3.06	3.04	35
201	2.941	2.925	15
004	2.658	2.646	20
202	2.652		
211	2.650		
212	2.433	2.424	5
213	2.166	2.157	15
220	2.164		
005	2.126	2.112	5
221	2.120		
204	2.006	2.001	40
222	2.004		
310	1.935	1.931	5
115	1.908	1.900	15
214	1.907		
311	1.904		
223	1.847	1.842	5
312	1.819	1.814	35
006	1.772	1.763	10
205	1.746	1.734	10
313	1.698	1.693	5
215	1.679	1.673	25
224	1.678		
321	1.676		
116	1.640	1.634	20
322	1.617	1.614	10
314	1.564	1.555	5
206	1.533	1.528	5
323	1.531		
400	1.530		
007	1.519	1.512	10
225	1.516		
401	1.514		
216	1.487	1.483	10
402	1.470	1.467	10
411	1.470		
117	1.433	1.429	5
315	1.431		
324	1.430		
412	1.430		
331	1.429		
332	1.392	1.390	5
226	1.371	1.369	5
413	1.369		
420	1.368		
207	1.360	1.356	5
421	1.357		
008	1.329	1.325	10
217	1.328		
325	1.326		
404	1.326		
422	1.325		
316	1.307	1.305	15
414	1.296	1.294	10

[a] Philips 114.6 mm. diameter powder camera, Straumanis mounting; λ(Cu Kα) = 1.5418 Å. [b] Relative peak intensities above background from densitometer measurements.

TABLE II

PARTIAL POWDER X-RAY DIFFRACTION PATTERN OF BERYLLIUM DIIODIDE, FORM II

HKL[a]	*hkl*[b]	*d*, Å.		I/I_1[d]
		Calcd.	Obsd.[c]	
111	042	3.392	3.37	100
	402	3.362	3.35	55
200	440	2.933	2.92	30
	004	2.907	2.89	60
220	080	2.088	2.080	45
	444	2.065	2.058	60
	800	2.060		
311	482	1.774	1.772	35
	842	1.761	1.752	70
	046	1.758		
	406	1.754		
222	084	1.696	1.691	10
	804	1.681	1.675	15
400	880	1.4663	1.463	10
	008	1.4536	1.453	20
331	0·12·2	1.3535	1.352	20
	486	1.3428	1.340	5
	846	1.3372	1.336	25
	12·0·2	1.3364		
420	4·12·0	1.3187	1.318	5
	884	1.3092	1.307	5
	12·4·0	1.3046		
	448	1.3023	1.301	20
422	4·12·4	1.2008	1.201	5
	088	1.1929	1.189	10
	12·4·4	1.1904		
	808	1.1879		
333, 511	8·12·2	1.1314	1.131	5
	0·12·6	1.1305		
	12·8·2	1.1256	1.119	5
	12·0·6	1.1207		
	0·4·10	1.1203		
	4·0·10	1.1194		
440	0·16·0	1.0439	1.032	5
	888	1.0323		
	16·0·0	1.0300		
531	4·16·2	0.9969	0.9979	5
	8·12·6	.9911		
	12·8·6	.9873	0.9856	10
	4·8·10	.9864		
	16·4·2	.9855		
	8·4·10	.9842		
600, 442	0·16·4	.9824	0.9776	<5
	12·12·0	.9775		
	4·12·8	.9767		
	12·4·8	.9709	.9704	5
	16·0·4	.9709		
	0·0·12	.9691		

[a] Indices of the face-centered-cubic pseudocell derived from the true cell by the transformation 1/4, 1/4, 0/1/4, $\bar{1}/4$, 0/0, 0, 1/2. [b] Indices of the true, orthorhombic unit cell. [c] Philips 114.6 mm. diameter powder camera, Straumanis mounting; λ(Cu Kα) = 1.5418 Å. [d] Relative peak intensities above background from densitometer measurements.

approximate body-centered arrangement of iodine ions. Further, the ratios of c_0' to a_0' and b_0' (1.41 and 1.39, respectively) approximate the square root of two. By the transformation 1, 1, 0/1, $\bar{1}$, 0/0, 0, 1 the above body-centered arrangement of iodine ions may be described as a face-centered-monoclinic arrangement with unit dimensions $a_0'' = 5.866$, $b_0'' = 5.866$, $c_0'' = 5.815$ Å., $\gamma = 90° 46'$. This may be regarded as a distorted face-centered-cubic arrangement of iodine ions, *i.e.*, a distorted cubic-closepacked arrangement. The relation between the true orthorhombic unit cell and the cubic pseudocell is apparent in Table II. Calculated and observed *d* spacings are closely grouped corresponding to possible spacings of the face-centered-cubic pseudocell.

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[CONTRIBUTION FROM THE IBM WATSON LABORATORY AT COLUMBIA UNIVERSITY]

Chemistry of the Group VB Pentoxides. VI. The Polymorphism of Nb_2O_5

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The polymorphism of Nb_2O_5 has been reinvestigated. Experimental results indicate the definite existence of two modifications and the possible existence of a third. The δ-modification recently reported has been shown to be a poorly crystallized state of the γ-phase. It is proposed that the α- and β-phases are identical, with the β-modification existing as a two-dimensional array. Transformation temperatures were found to be: amorphous to γ 435°, γ to α 830°. The densities are: amorphous 4.36 g./cm.^{3} at 25°, γ, 5.17 g./cm.^{3} at 25° and α, 4.55 g./cm.^{3} at 25°. None of the transformations was reversible. The α-phase was reindexed on the basis of a monoclinic unit cell with a = 21.34 Å., b = 2.816 Å., c = 19.47 Å. and $\sphericalangle \beta = 120°20'$ having 14 molecules/unit cell and an X-ray density of 4.52 g./cm.^{3}. The freezing point of Nb_2O_5 obtained in the study was 1491°.

Previous investigations pertaining to the chemistry of the Group VB pentoxides and their reactions with alkali oxides and carbonates have included studies of the polymorphism of Ta_2O_5[1] and V_2O_5.[2] Examination of the temperature–phase relationships of Nb_2O_5, in addition to completing the study of the comparative polymorphism of the pentoxides, may help explain the non-model behavior exhibited by the systems $K_2O–Ta_2O_5$[1] and $K_2O–Nb_2O_5$.[3]

In 1941, Brauer[4] reported that Nb_2O_5 existed in three crystalline modifications having the following transformations: amorphous to γ 500°, γ to β 1000° and β to α 1100°.[5] In 1951, Hahn[6] published X-ray data for an unspecified form of Nb_2O_5. The pattern did not correspond to Brauer's α-, β- or γ-forms. Subsequently Schäfer, *et al.*,[7,8] presented the results of a partial X-ray investigation of the system $Nb_2O_5–Ta_2O_5$ in which a study of the polymorphism of Nb_2O_5 was included. This work confirmed the α-, β- and γ-polymorphs reported by Brauer: however, the transformation temperatures were significantly different. Furthermore, contrary to evidence given by Brauer, the γ to β transformation was found to be reversible. The reversibility of the α to β transformation was not clarified. Schäfer also observed that the crystallization of the amorphous oxide sometimes results in a mixture of β- and γ-Nb_2O_5. Lapitskiĭ, *et al.*,[9] showed with thermal analysis that the amorphous pentoxide exhibited an exotherm at 609°. The temperature of this heat effect is not coincidental with any of the reported transition temperatures. Recently, Frevel and Rinn[10] reported a δ-form which was indexed on the basis of a pseudohexagonal unit cell. The δ-form is apparently converted to the γ-phase at 700°, a contradiction of Brauer's results. The method of preparation of the δ-form was not specified.

In order to resolve the uncertainties concerning the number of polymorphs of Nb_2O_5, and the temperatures and reversibilities of transformations between phases, it was felt that a complete re-evaluation of previously reported data was in order.

Experimental Procedure

Preparation of Reagents.—Sublimed $NbCl_5$ prepared from high purity niobium[11] was used for the preparation of Nb_2O_5. The pentachloride was hydrolyzed in distilled water and the precipitated Nb_2O_5 was washed until the filtrate was free of chloride ion. The washings, with intermediate digestions at boiling temperatures, were continued through five further cycles. After drying for 24 hours at 100° the pentoxide was found to be amorphous to X-rays. The excessive washing and digestion treatment was employed because, as will be shown, the transformation temperatures of the different pentoxide phases were impurity sensitive.

"High Purity"[12] Nb_2O_5 was used in experiments designed to determine the reversibility of phase transformations. Prior to use the oxide was heated at 1200° for 24 hours to ensure complete conversion to the high temperature form. A portion of the Nb_2O_5 was fused with K_2CO_3, dissolved in water and amorphous hydrated Nb_2O_5 was precipitated as described in an earlier paper.[13] X-Ray analysis indicated that this material was also amorphous.

Differential Thermal Analysis.—A large number of furnaces specifically designed for heating curve analysis have been described in the literature. The general construction involves the use of a mobile furnace which rolls into position over a fixed sample holder and thermocouple assembly. The holder and thermocouple assembly are often difficult to clean and frequently require refabrication for each analysis. In addition the apparatus is costly, requiring elaborate engineering. The problems inherent in the standard

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[1] A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, THIS JOURNAL, **78**, 4514 (1956).

[2] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **78**, 1536 (1956).

[3] A. Reisman and F. Holtzberg, *ibid.*, **77**, 2115 (1955).

[4] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

[5] Consistent with accepted nomenclature, the highest temperature phase will be denoted as α which corresponds to Brauer's "Hochform."

[6] R. B. Hahn, THIS JOURNAL, **73**, 5091 (1951).

[7] H. Schäfer and G. Breil, *Z. anorg. allgem. Chem.*, **267**, 265 (1952).

[8] H. Schäfer, A. Durkop and M. Jori, *ibid.*, **275**, 19 (1954).

[9] A. V. Lapitskiĭ, Y. P. Simanov and E. I. Yarembash, *J. Phys. Chem. Moskav*, **26**, 56 (1952).

[10] L. K. Frevel and H. N. Rinn, *Anal. Chem.*, **27**, 1329 (1955).

[11] The $NbCl_5$ was obtained from the A. D. Mackay Co. The niobium from which the pentachloride was prepared was Fansteel High Purity Grade containing a maximum impurity of 0.2% Ta.

[12] The high purity of Nb_2O_5 was obtained from the Fansteel Metallurgical Co. and contained as a maximum impurity 0.2% Ta.

[13] (a) A. Reisman, F. Holtzberg, S. Triebwasser and M. Berkenblit, THIS JOURNAL, **78**, 719 (1956); (b) See Errata for ref. 11 in THIS JOURNAL, **78**, 6423 (1956).