As an oxidant, perbromate exhibits properties intermediate between those of perchlorate and those of periodate. However, because of their slowness, the reactions shed little or no light on the thermodynamic stability and oxidizing power of perbromate.

The instability of concentrated perbromic acid warrants detailed study to elucidate the mechanism of decomposition. It is interesting to note that some perbromic acid can be distilled in spite of this decomposition, confirming the early observation of vapor-phase $HBrO_4$ in the mass spectrometer.[11]

The properties found for the perbromates do not explain why these compounds have been so hard to prepare. Although the thermal decomposition studies show that efforts to make perbromates by disproportionation of bromates are most likely doomed to failure, it is not at all clear why electrolytic synthesis is so unsatisfactory.[2] It may be that the stumbling block is a prohibitively high activation energy caused by an extremely unstable Br(VI) intermediate through which the synthesis must proceed.

Acknowledgment—The author is indebted to Mr. Frank Gallagher and Mr. William Johnson for the thermogravimetric measurements, to Mr. Kenneth Jensen for the potassium analyses, to Mrs. Donald Engelkemeir for measurement of oxygen isotope ratios, and to Mr. Jerome Lech for the analyses by emission spectrography.

---

[11] M. H. Studier, *J. Am. Chem. Soc.*, **90**, 1901 (1968).

CONTRIBUTION NO. 2359 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

The Lower Halides of Hafnium. A Nonstoichiometric Hafnium Triiodide Phase[1]

BY ARTHUR W. STRUSS AND JOHN D. CORBETT

Received July 5, 1968

A hafnium iodide phase of the composition $HfI_{3.2-3.3}$ which is free of unreacted metal is obtained by the reaction of liquid HfI_4 with metal foil (600 ppm of Zr) in a sealed tantalum container at 500–550°. The lower composition limit established from equilibration with separate metal powder is $HfI_{3.0_0}$ at 425–575°; the phase in equilibrium with HfI_4(l) varies from $HfI_{3.4_6}$ at 475° to $HfI_{3.2_0}$ at 550°. Neither equilibration of HfI_4 or HfI_3 with metal at up to 1000° nor disproportionation of HfI_3 under high vacuum gives any indication of the existence of still lower iodide, specifically HfI_2. X-Ray powder data indicate that the *a* and *c* dimensions of the previously suggested hexagonal unit cell[2] should probably be doubled and quadrupled, respectively. The composition $HfI_{3.3_5}$ shows a small temperature-independent paramagnetism corresponding to a μ_{eff} value of 0.68 at 300°K; the susceptibilities are considerably smaller than reported earlier[3] for impure samples.

Introduction

The lower halides of hafnium have been only partially characterized, principally because reductions of the tetrahalides under diverse conditions are characteristically slow and incomplete. To some extent the interpretation of what is known has been based on the assumption that there should be a close parallel with the better known lower halides of zirconium as there is in many ways in the chemistries of the tetravalent states. The latter, of course, arises from the well-known effect of the lanthanide contraction, at least as it affects properties largely determined by radii of the tetrapositive state, but it is less clear how the interjection of the 4f elements should influence the stabilities of lower oxidation states.

The direct reduction of hafnium(IV) to hafnium(III) halides (except fluoride) by hafnium metal itself has been brought to completion best by Larsen and Leddy.[4] Stoichiometric amounts of tetrahalide and metal powder sealed in glass ampoules were heated up to 700° using a bomb to counteract the internal pressures. This procedure gave up to 80–85% conversion to the tribromides and triiodides of both hafnium and zirconium but only about 40% for the chlorides. The unreacted tetrahalide sublimbed off during the quenching process, and solutions of the residues in water gave appropriate analyses for the trihalides after a precipitate of unreacted metal was filtered off. Trihalides of greater than 99% purity were obtained when the initial products were reground and reheated with large excesses of the appropriate tetrahalide, although analytical data were not reported. In later work such an HfI_3 product was found to contain a residue of 6.4% metal, with larger amounts in the chloride and bromide.[2] The hafnium (and zirconium) trihalides all appeared to disproportionate incompletely into gaseous tetrahalide and a presumed dihalide when heated above 450° in sealed, evacuated tubes, and the reaction was followed either by tetrahalide loss or in a high-temperature X-ray camera.[4] The same synthesis reactions at 37–60 atm and *ca.* 500° gave ≥99% conversion to the zirconium(III) chloride and bromide[5,6] but unreproducible compositions with

---

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 8–13, 1968.

[2] L. F. Dahl, T. Chiang, P. W. Seabaugh, and E. M. Larsen, *Inorg. Chem.*, **3**, 1236 (1964).

[3] W. A. Baker, Jr., and A. R. Janus, *J. Inorg. Nucl. Chem.*, **26**, 2087 (1964).

[4] E. M. Larsen and J. J. Leddy, *J. Am. Chem. Soc.*, **78**, 5983 (1956).

the same hafnium halides.[7] In contrast to the present results, the reaction of excess ZrI_4 with a metal sheet at 510° resulted in a nonadhering ZrI_3 product and this under effusion conditions first disproportionated to $ZrI_{2.86}$ and then to ZrI_2.[8]

Aluminum has also been used as the reductant following its application in the zirconium systems. Aluminum with excess $HfBr_4$ in a bomb at 60 atm and 470° for 100 hr gave pure hafnium(III) bromide (Br/Hf = 3.00–3.03) in 1–1.5-g amounts after removal of the $AlBr_3$ and excess $HfBr_4$ by sublimation.[7] On the other hand, the product of the reduction of HfI_4 with aluminum powder at only 350–385° for 2–14 days followed by a like sublimation still contained unreacted aluminum, and the material gave μ_{eff} values in excess of the spin-only value for a d^1 salt.[3]

Dahl, *et al.*,[2] interpreted X-ray powder data for zirconium(III) chloride, bromide, and iodide and hafnium(III) iodide in terms of a common structure, the β-$TiCl_3$ type. In this the formally octahedral holes between hcp halogen atoms are occupied such that infinite chains of MX_6 octahedra sharing opposite faces are oriented parallel to the c axis. The metal atoms are evidently equally spaced in the chains according to the extinction of $h0l$ reflections with $l \neq 2n$. Watts[9] has confirmed this condition for β-$ZrCl_3$. A basically similar structure has also been reported for TiI_3 by von Schnering[10] although very weak superlattice diffractions found with single-crystal (but not powder) methods require a doubling of the a axis.

In the present study hafnium metal foil has been used as the reductant to allow ready physical separation of an uncontaminated triiodide phase from unreacted metal. The results show that (1) hafnium(III) iodide is the only reduced iodide, (2) the phase has a substantial homogeneity range on the hafnium(IV) side, and (3) the triiodide gives X-ray and magnetic susceptibility results somewhat different from what have been reported previously.

Experimental Section

Materials.—Crystal bar hafnium (Nuclear Materials and Equipment Corp.) was used in much of the preliminary work. This had listed impurities of 3% Zr and, in ppm: C, ~50; H, ~12; O, ~50; Mo, 30; Si, 40, with other metallic elements below the limit of spectrographic detection. The metal was cold rolled into 10–15-mil foil for the preparation of HfI_3. The larger surface area of 325-mesh powder (Wah Chang) was employed for low-limit equilibrations; this contained, in ppm: O, 790; N, 121; C, <30; H, 64; Al, 97; Cr, 15; Fe, 96; Ti, 37.

The fractionation of the zirconium impurity in the above material is a substantial problem in certain reactions and so final parameters of the system were obtained with hafnium containing 600 ppm of zirconium (Leico Industries). The first batch (O, 420; N, 124; C, 320 ppm) was arc-melted, hot-rolled to foil while clad in stainless steel, and then electropolished after the cladding had been stripped off. A second sample of the metal containing 1600 ppm of O, 609 ppm of N, and 310 ppm of C could not be rolled to satisfactory foil but a very satisfactory 1–3-mil layer was obtained by vacuum sublimation onto 5-mil tantalum sheet.

Hafnium tetraiodide was prepared by reaction of the metal at 500° with iodine at ~1 atm in an evacuated Pyrex tube. The yellow-orange product was purified by sublimation under vacuum ($\leq 10^{-5}$ Torr) at 200–250°; the melting point was 455 ± 1°. The metal powder and all iodide samples were stored in evacuated containers, and all transfers were carried out in an argon-filled drybox.

Hafnium Triiodide Syntheses.—The triiodide phase was prepared by reaction of HfI_4 with metal foil in a sealed tantalum tube at 500–550°, the latter being the maximum temperature at which the 15-mil container could reliably withstand the vapor pressure of liquid HfI_4 (~20 atm). A 1–1.5-mil layer of triiodide phase on the metal was obtained after a few days and this was easily scraped off with another piece of hafnium and then freed of excess HfI_4 by heating under high vacuum at 150–200°. The process typically yielded 3–5 g with an I/Hf ratio of 3.3–3.2.

The upper and lower limits of the composition range of the phase were established by equilibration of the synthesis product with liquid HfI_4 and with metal, respectively, there being no still lower iodide phase to interfere with the latter (*vide infra*). The salt phase held in a loosely crimped 6-mm diameter tantalum tube within a 12-mm tube containing the metal powder was equilibrated for 3–18 days. About 20 g of metal/g of salt was necessary to prevent the triiodide produced from blocking the metal surface. The metal in the reservoir gave weak diffractions for the triiodide phase after the equilibration and was regenerated after each run by heating under vacuum at 550–600°. For the upper limit, reduced salt and excess liquid HfI_4 were heated together for 3–12 days, and the excess HfI_4 thereafter was removed under vacuum at 170–180°. Because of the large amount of HfI_4 removed, care must be taken to avoid contamination which leaves HfO_2 or an oxyiodide in the product. Flakes of these impurities are readily detected under the microscope. The upper and lower limits begin to lose HfI_4 under vacuum at about 220–230 and 275°, respectively, although the former are in equilibrium with the tetraiodide at the equilibration temperature.

Numerous attempts were made to synthesize still lower hafnium iodides. Isothermal equilibrations of $HfI_{3.3}$ with metal were studied using *ca.* 0.2 g of salt and 2 g of foil in sealed tubes. Also, the disproportionation of $HfI_{3.3}$ in a tantalum crucible under high vacuum was followed by the HfI_4 weight loss. The capped, 25 × 25 mm crucible employed had a short, open length of 9-mm tubing welded through one end so that a plastic cap could be fitted over this and the container then removed from the drybox and weighed without contamination. The cap was held in place by a "C" clamp during reentry through the evacuable lock of the drybox.

X-Ray Data.—Powder diffraction data were obtained with samples sealed in 0.3-mm Lindemann capillaries, a 114.6-mm Debye–Scherrer camera, and nickel-filtered copper Kα radiation. Corrections for film shrinkage and for absorption (based on an internal KI standard) were applied for all quantitative comparisons. The hexagonal cell parameters were calculated by averaging the data calculated from the pairs of lines (523) and (413), (415) and (115), (604) and (304) for a and (523) and (521), (413) and (412), (415) and (413), (415) and (412) for c. The value of θ varies between 36 and 61° for these, and no absorption correction was indicated. No systematic variation of the parameters obtained was evident.

Magnetic Data.—These were obtained as before[11] at 78–300°K using a 4.580-mm i.d. Gouy tube and fields of 5–9.5 kG. The data were corrected for core diamagnetism using Selwood's values.

---

[5] H. L. Schläfer and H. Skoludek, *Z. Anorg. Allgem. Chem.*, **316**, 15 (1962).

[6] H. L. Schläfer and H.-W. Wille, *ibid.*, **327**, 253 (1964).

[7] H. L. Schläfer and H.-W. Wille, *ibid.*, **351**, 279 (1967).

[8] F. R. Sale and R. A. Shelton, *J. Less-Common Metals*, **9**, 60, 64 (1965).

[9] J. A. Watts, *Inorg. Chem.*, **5**, 281 (1966).

[10] H. G. von Schnering, *Naturwissenschaften*, **14**, 359 (1966).

[11] R. A. Sallach and J. D. Corbett, *Inorg. Chem.*, **3**, 993 (1964).

Analyses.—Hafnium(IV) iodide was both weighed and dissolved in water in an evacuated container so as to avoid loss of HI. The metal value was determined by back-titration at pH 2.0 of excess added EDTA with standard $Bi(NO_3)_3$ and 0.7 g of thiourea as the indicator. Iodide was titrated using eosin Y indicator. Eight determinations gave an average I/Hf ratio of 4.00 ± 0.01 for the tetraiodide with an average recovery of 99.82%.

Addition of water to reduced hafnium samples always produced some finely divided and partly colloidal metal. The amount so obtained, a few per cent of the total sample weight, was greater at the upper composition limit of the phase and was inversely dependent on the amount of water used. Since metal was never detected in the anhydrous samples, its production here was attributed to disproportionation during the solution process. Analytical samples were weighed under argon in tightly capped, 70-ml polyethylene bottles after which 40 ml of dilute HF (1 vol % of 48%) was added, and the bottle was quickly recapped to prevent loss of HI. The metal formed redissolved rather readily. At this point some of the samples also contained a small amount of a brown precipitate of crystalline HfO_2, up to 0.2 wt % of the total sample. The color was characteristic of the material which had been heated, as opposed to the white precipitate obtained from aqueous solution, and so this material was concluded to represent an oxide contaminant in the original sample. In early work the precipitate was usually taken into solution in 48% HF and then added to the remainder of the sample. This level of oxide contamination affects the I/Hf ratio by ≤ -0.02 and is therefore negligible. In a few cases 1–5% oxide was found, particularly after upper-limit equilibrations when contamination of the HfI_4 was more likely because of leaks in the tantalum containers. Such HfO_2 reacted with excess HfI_4 to form oxyiodides very slowly; the latter were more frequently encountered in reactions of HfI_4 with traces of oxygen or moisture at lower temperatures.

Since the HF present interfered with EDTA titration, hafnium cupferrate[12] was precipitated from an aliquot in 10% H_2SO_4, filtered, and ignited to the oxide. The precipitate was much easier to handle if only sufficient cupferron reagent was added to give coagulation. Analysis of three standard hafnium solutions by this procedure gave positive errors of 0.49, 0.39, and 0.55%. Prior recrystallization of the cupferron from 95% ethanol or precipitation of the cupferrate from 10% hydrochloric acid did not eliminate the error. Although prior workers[12] have attributed such positive errors to traces of K_2SO_4, fluoride may have been responsible here. The recoveries for all reduced samples were in the range of 99.3–101.3% and were generally between 100.0 and 100.6%.

The zirconium contents of the ignited oxides were determined to $\pm\sim 5\%$ by emission spectrometry; data for samples containing more than 5% Zr were also obtained (by difference) by activation analysis. Fractionation in samples prepared from 3% material was often substantial and could not be neglected. In disproportionation for example, an initial HfI_{3+} salt containing 4 ± 0.5% Zr in the metal portion produced HfI_4 with 1 ± 0.5% Zr (less during the initial stages), leaving 67.0 ± 0.2% Zr calculated for the metal residue (5.3 wt % of the original sample). Emission spectrometry also verified the suitability of the tantalum containers. Tantalum was not detected in the reduced iodide phases or in the metal or HfI_4 produced by decomposition, and hafnium was not found in the walls of the container.

Results

The amount of the triiodide phase which may be recovered from the metal foil after the reaction with liquid tetraiodide is only a small fraction of theory and very dependent on the surface area of the metal. The yields are greatest at 500–550° where the I/Hf ratios in the product vary from 3.35 to 3.2, respectively. These compositions are near the upper limit of a substantial composition range for the phase. The results of isothermal equilibrations of the initial salt with metal powder and with liquid HfI_4 to give the lower and upper compositions limits, respectively, are shown in Figure 1 as a function of temperature. In all cases the I/Hf ratios are uncertain by about ±0.04 and would in most cases be raised by about this amount if allowance were made for the small but persistent error in the hafnium analysis (see the Experimental Section). As the data stand, the lower limit of the phase is $HfI_{3.0_0}$ between 425 and 575°. As expected, the upper limit shows a marked dependence on temperature, varying from about I/Hf = 3.2_0 at 550 to 3.4_6 at 475°. The more limited temperature range covered here is dictated by the problem of containment at the upper end and by the slowness of the reaction at the lower. At 425° significant changes in the composition of samples with initial ratios of 3.33–3.5 were not obtained in up to 13 days, and at 455° an increase in the ratio from 3.3 to only 3.41 was achieved in a like period. The compositions obtained at 525 and 550° were approached from both directions in order to ensure that equilibrium was indeed being achieved, and part of those at 500° were obtained starting with $HfI_{3.0}$. Although a step function could be imagined to describe the somewhat scattered upper-limit data shown in the figure, there is no support for discrete compositions in the X-ray data to be presented later.

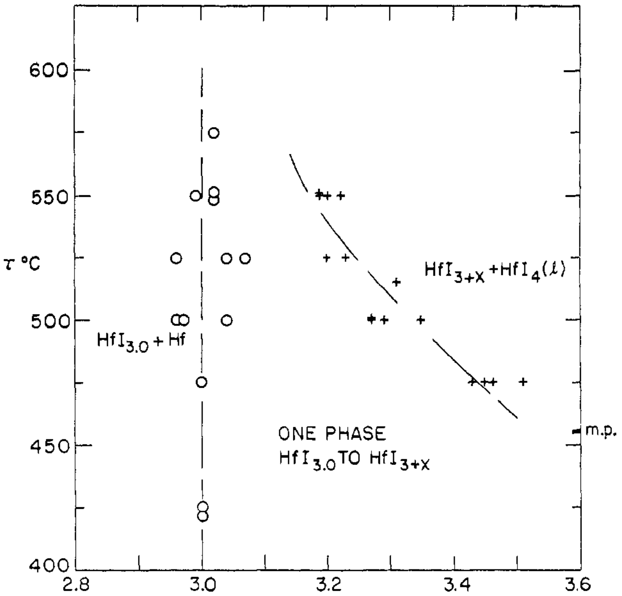

Figure 1.—The lower and upper composition limits for the nonstoichiometric hafnium triiodide phase as functions of temperature.

The fact that the compositions of the triiodide phase formed in the synthesis reaction agree fairly well with the upper-limit data suggests indicating that the slow step is probably oxidation and diffusion of the metal. The yield at 550° is also less than 500°, as is the width

---

[12] P. J. Elving and E. C. Olson, *Anal. Chem.*, **27**, 1817 (1955).

of the homogeneity range and, presumably, the concentration of vacancies important for metal diffusion in the salt. No evidence for solution of the triiodide phase in liquid HfI_4 was noted.

The above data pertain to samples containing 0.04–0.25% zirconium and are therefore taken to be representative of the chemistry of the pure element. When the initial reactants contain 3% zirconium, the lower limit contains 4–14% zirconium, and the upper, up to 30%, both depending on the relative amounts of the reactants employed and the extent to which the tetraiodide has been reused. Correspondingly, the I/(Hf + Zr) ratios at 550° in the salt as prepared and for the upper limit are both 0.1–0.2 higher ($MI_{3.4-3.5}$) than obtained with higher purity hafnium, in proportion to the amount of zirconium present.

Many diverse experiments have led to the conclusion that no additional phase exists between $HfI_{3.0}$ and the metal. Attempts to ensure that a sluggish equilibrium was not responsible for any omission included equilibrations of triiodide alone with separate hafnium foil at 700–1000° for 1–8 days and of the triiodide as prepared on foil for several days at 675°. In all cases the amount of reaction with the foil was very slight, and metal was the only new product in the salt sample according to X-ray data. The metal arises because some disproportionation of HfI_3 is necessary under the conditions used in order to establish what is an appreciable equilibrium pressure of $HfI_4(g)$. In no experiment was there any evidence for a vapor-phase transport of HfI_3. Reductions of HfI_4 by aluminum wire, such as at 500° for 4 days, were uniformly unsuccessful as was such a reaction in the presence of an AlI_3 flux at 500°. The very limited reaction appears to result because of the formation of a thin layer of the stable $HfAl_3$ phase on the metal, as identified by its powder pattern.[13] The yield from the usual Hf–HfI_4 synthesis reaction at 500° is about doubled in the presence of AlI_3. The results with AlI_3 are in some contrast with the more ready reactions of the corresponding zirconium system.[14]

The slow disproportionation of HfI_3 under high vacuum at 300–400° was also studied as a route to a potential new phase although in general such nonequilibrium processes at relatively low temperatures may not be especially definitive. Generally the powder pattern of the triiodide persisted to I/Hf < 0.4, and metal was the only solid product. Occasionally poor-quality diffractions of a new phase also appeared, though at widely varying compositions, but in these cases much higher temperatures (600–700° *vs.* 375–400°) were necessary to complete the HfI_4 evolution, and HfO_2 (plus metal) was *always* found in the final product. The extra phase is therefore concluded to be an oxyiodide contaminant formed during the long reaction times which were employed.

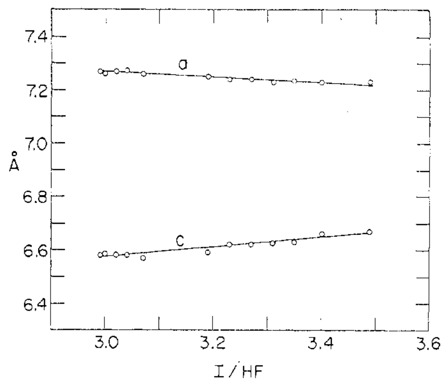

Figure 2.—The hexagonal subcell parameters *a* and *c* of the hafnium triiodide phase as functions of composition. The correct parameters are apparently two and four times larger, respectively (see text).

The "triiodide" as prepared is dark violet to black and does not show a discernible color change on reduction through the homogeneity range to $HfI_{3.0}$. The change to dark green on grinding is totally without effect on the diffraction pattern and is concluded to result just from a change in particle size. Well-formed rose-red crystals are obtained when metal from which a preparation has been scraped is equilibrated with $HfI_{3.3}$ at 675°, although these turn out to be polycrystalline bundles.

The electrical resistance of the phase as prepared on foil or as a pressed pellet is typical of a large gap "salt" although conduction in only one dimension[2] might be difficult to establish in this way. The reflectance spectrum of $HfI_{3.3}$ (diluted with KI) contains two bands at 38.5 and 29 kK, plus a broad band starting at about 14.3 kK and extending beyond 11 kK. The broad minimum near 20 kK is thus responsible for the green color. The spectral properties show a definite correspondence with those reported for zirconium(III) and hafnium(III) chlorides and bromides.[7] The composition $HfI_{3.3_5}$ (5% Zr) exhibits only a small temperature-independent paramagnetism between 78 and 300°K. The χ_P value of 1.6×10^{-4} cgsu mol^{-1} (at 5.05 kG) corresponds to $\mu_{eff} = 0.62\ \beta$ at room temperature. The small field dependence found, −2.8% kG^{-1} in χ_P between 5.05 and 9.50 kG, may have originated with traces of nickel in the metal employed.

The X-ray data obtained for the triiodide phase include all of those found earlier[2] save for two very weak lines which were not observed here ($1/d^2$ = 0.3906, 0.9075). Unit cell parameters calculated for the earlier hexagonal cell are shown in Figure 2 as a function of composition: *a* decreases from 7.27 to 7.23 Å and *c* increases from 6.58 to 6.67 Å (all ±0.01 Å) as the composition varies from $HfI_{3.00}$ to $HfI_{3.49}$. The previous data yielded $a = 7.225$ and $c = 6.59$ Å.

The relatively long equilibration times necessary for the study of the phase breadth resulted in samples which gave excellent powder patterns extending through the back-reflection region. These were particularly sharp at the lower compositions, and α_1–α_2 doubling

---

(13) A. E. Dwight, J. W. Downey, and R. A. Conner, Jr., *Acta Cryst.*, **14**, 75 (1961).

(14) F. Gil-Arnao and E. M. Larsen, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 138.

was at times discernible as low as 30° (θ). With this advantage a substantial number of additional lines were observed which were not noted in the previous study.[2,15] More important, reflections were also noted which were inconsistent with the extinctions required by the previous space group or which did not fit the hexagonal unit cell given. However, the latter group are evidently superlattice diffractions as they all may be accounted for with simple fractional indices (or simple multiples of the unit cell dimensions). Table I lists the additional data according to the approximate composition range for their observation, their relative intensities, and the observed and calculated values of $1/d^2$ for the indicated indices. All lines were observed on at least two of fifteen compositions examined. The quality of the patterns decreases with increasing iodide content so the upper limits of observation for some may not be as significant. The new lines listed are certainly not associated with oxide impurities. The disputed[2] (001) reflection was not found. An arc suggestive of (001) yielded inconsistent parameters and was concluded to be a result of absorption doubling of (100) since its relative position varied with capillary size, and it was absent in a Guinier pattern.

TABLE I

SIGNIFICANT NEW LINES IN THE POWDER PATTERNS OF $HfI_{3.0-3.5}$

Range obsd, I/Hf	I^a	*hkl*	$1/d^{2\,b}$ Obsd	Calcd
3.2±	<5	$10^{1}/_{2}$	0.0315	0.0311
3.2–3.5	<5	$10^{3}/_{4}$	0.0382	0.0383
3.4–3.5	5	101	0.0496	0.0480
3.2–3.5	5–10	$11^{1}/_{4}$	0.0780	0.0778
		$10^{3}/_{2}$		0.0767
3.0–3.5	5–10	$11^{1}/_{2}$	0.0821	0.0821
3.0	5	$11^{3}/_{4}$	0.0853	0.0887
3.0	5	$1^{1}/_{2}{}^{3}/_{2}$	0.0969	0.0961
3.0–3.4	5–15	$20^{3}/_{4}$	0.1153	0.1146
3.2–3.45	<5	$11^{3}/_{2}$	0.1276	0.1277
3.4–3.5	<5	$1^{1}/_{2}2$	0.1382	0.1346
3.1–3.5	<5–15	$2^{1}/_{2}1$	0.156	0.1564
3.0–3.4	≤5	$21^{1}/_{2}$	0.188	0.183
3.0–3.5	<5–15	003	0.204	0.204
3.2–3.5	<5	$11^{5}/_{2}$	0.218	0.219
3.0–3.5	5	301	0.252	0.252
3.0–3.5	≤5	$1^{3}/_{2}{}^{5}/_{2}$	0.267	0.262
3.5	<5	*c*	0.308	
3.35–3.5	<5	*c*	0.313	
3.2–3.5	5	$22^{3}/_{2}$	0.358	0.357
3.1–3.2	5	*c*	0.394	
3.0–3.5	<5	*c*	0.457–0.445	
3.0	<5	*c*	0.493	

[a] Based on 100 for the strongest diffraction. Changes in intensity given refer to increasing I/Hf. [b] At I/Hf = 3.0, 3.23, or 3.49, using appropriate lattice constants at that composition from Figure 2. [c] Indexing was not attempted.

Discussion

The present results indicate that $HfI_{3.00}$ is in equilibrium with the metal and is therefore the lowest hafnium iodide, subject only to the condition that any other phase be kinetically accessible at not greater than 1000° in reactions of metal and HfI_4(g). Earlier X-ray evidence to the contrary may have instead been the result of contamination from attack of the glass containers, which becomes appreciable near 600°. If the large iodide ion represents the most favorable anion for the stabilization of low oxidation states here as it usually does, the existence of any dihalide of hafnium is doubtful, in contrast with the stability of at least $ZrBr_2$[16] and ZrI_2.[8] There is no substantial evidence for a marked homogeneity range in the other trihalides of the titanium family, although obvious complications associated with many synthetic approaches could make the identification of the equilibrium properties of any phase difficult. The temperature dependence of the upper-limit composition (Figure 1) is opposite to what is usually found for homogeneity regions. However, the temperatures involved here are substantially lower than usual so perhaps the enthalpy rather than the entropy change is controlling.

The color of the triiodide observed here and elsewhere,[3] black to dark green depending on particle size, is at variance with another report of a brown product.[4] Such a color is produced (together with iodine) by exposure to traces of moist air, as has also been observed with $ZrCl_3$.[17] Also, some of the colored, aqueous solutions of trihalides which have been thought to contain zirconium or hafnium(III) solutes may have resulted from the colloidal oxide (or metal), which is brown to orange-brown when formed from HfI_3.

X-Ray data obtained for the hafnium iodide phase require some modification of the structure proposed earlier.[2] There seems to be little doubt that three observed diffractions violate the proposed *h0l* condition ($l = 2n$) and that a considerable number of others apparently require that the cell have a doubled a and a quadrupled c dimension. However, the additional lines are all weak at the $HfI_{3.0}$ limit so that the basic structure proposed is probably still close to correct. A number of additional lines (or changes in intensities) arise on oxidation of the phase to $HfI_{3.5}$, but these are by and large relatively weak (or small). We are inclined to view the process in terms of the cation substitution $4Hf^{3+} = 3Hf^{4+} + \square$, and the onset of new lines in the process suggests that the products may be at least partially ordered. The one-phase oxidation would substantially amount to the substitution of smaller metal–metal-bonded strings or groups for the infinite chains proposed for the structure at the lower limit. The gross changes in lattice dimensions on oxidation are consistent with this general proposition. Thus the cross-sectional dimension of the shared "octahedra" and hence also a is decreased by the substitution while the reduction of the metal–metal bonding within the chains causes c to increase. The alternate interstitial substitution of iodide does not seem nearly as reasonable.

---

(15) For example, (110) (I = 5/100), (221) (35), (114) (5), (332) (5), (422) (5), (512) (15), (216) (10), (610) (5), (226) (10), (533) (10), (711) (5), (336) (10).

(16) H. L. Schläfer and H. Skoludek, *Z. Elektrochem.*, **66**, 367 (1962).

(17) I. E. Newnham and J. A. Watts, *J. Am. Chem. Soc.*, **82**, 2113 (1960).

The magnetic properties of HfI_3 reported previously[3] are at variance with those given here, apparently because of gross contamination of the earlier samples. The earlier results indicated $10^6\chi_g$ values of about 15.5 (green) to 11.2 (black) at 300°K and 5.2 kG, in contrast with only 0.27 found here for $HfI_{3.3_5}$ at 5.05 kG. The prior values of χ also showed a broad maximum near 120°K and substantially larger field and temperature dependencies. However, the samples employed were the residues from the incomplete reduction of HfI_4 with aluminum followed by sublimation of HfI_4 and AlI_3, and aluminum was evident in the powder patterns (together with seven unidentified lines.) In fact, the HfI_3 yield was only 5–10% for the green product and 12% for the black,[18] and the triiodide at best comprised 59–84% of the residue after sublimation. The hafnium analysis of the water-soluble portion was also quite low. Therefore it would appear that the high susceptibilities originated from more than HfI_3 and aluminum, perhaps hafnium–aluminum intermetallic phases. The present data for the triiodide phase are rather comparable with those obtained by Lewis, *et al.*,[19] for the zirconium(III) halides at only room temperature, which correspond to effective moments of about 0.4 β. The temperature-independent character of the small paramagnetism for the hafnium iodide phase is rather typical.

Acknowledgments.—Appreciation is expressed to a number of persons who provided significant assistance in this work: D. A. Lokken with the spectral and magnetic measurements, F. A. Schmidt and L. K. Reed with the preparation of metal foil, and E. L. DeKalb and K. L. Malaby with the zirconium analyses.

---

[18] A. R. Janus, Ph.D. Thesis, Syracuse University, 1964.

[19] J. Lewis, D. J. Machin, I. E. Newnham, and R. S. Nyholm, *J. Chem. Soc.*, 2036 (1962).

Contribution from the Department of Chemistry, Michigan State University,
East Lansing, Michigan 48823

Phase Analyses of Lanthanide Oxide Fluorides

By DENNIS B. SHINN[1] and HARRY A. EICK

Received July 10, 1968

Approximate composition limits and lattice parameters of the rhombohedral and tetragonal phases observed in the system $LnO_{1-x}F_{1+2x}$ (Ln = Nd, Gd, Er) are reported. Variation of the *c/a* ratio of the tetragonal phase with atomic number is noted and discussed. The rhombohedral to cubic transition temperatures of $LnO_{1-x}F_{1+2x}$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, and Er) determined from differential thermal analysis are reported and the transition is discussed. Thermal expansion data are reported for NdOF and its mode of thermal decomposition is indicated.

Introduction

Lanthanide oxide fluorides are often encountered as contaminants in metal trifluoride investigations, yet they have been studied only infrequently.[2–15] Zachariasen[2] reported for yttrium and lanthanum two oxide fluoride phases which he prepared by pyrohydrolysis of the fluorides: a rhombohedral LnOF and a tetragonal $LnO_{1-x}F_{1+2x}$ $(0.0 \leq x \leq 0.3)$. From an X-ray powder diffraction study he deduced that these phases were superstructures based upon fluorite in which the oxygen and fluorine atoms are ordered into distinct sites. In the bimolecular rhombohedral unit cell of LaOF, space group $R\bar{3}m$, he found the metal atoms to be at $\pm(XXX)$, where $X(\mathrm{La}) = 0.242$, and postulated that the anions were also situated along the threefold axis with $X(\mathrm{O}) = 0.370$ and $X(\mathrm{F}) = 0.122$. The value of α was 33.01° in contrast with the 33.56° value for fluorite based on a rhombohedral cell. Templeton[3] later concluded from a lattice energy calculation that the oxygen and fluorine atom positions should be interchanged. This rhombohedral structure has been observed[9,11–15] for most lanthanide oxide fluorides and values of α that vary between 33.0 and 33.3° have been reported.

The tetragonal phases exhibit space group Pnnm symmetry, and alternate layers of oxygen and fluorine atoms are normal to the *c* axis. The *c/a* ratios reported[2] for the lanthanum and yttrium tetragonal phases deviate slightly from 1.414, the value for cubic

---

[1] Abstracted in part from a thesis submitted by D. B. Shinn to the Graduate College of Michigan State University for the Ph.D. degree.

[2] W. H. Zachariasen, *Acta Cryst.*, **4**, 231 (1951).

[3] D. H. Templeton, *ibid.*, **10**, 788 (1957).

[4] W. Klemm and H. A. Klein, *Z. Anorg. Allgem. Chem.*, **248**, 167 (1941).

[5] F. Hund, *ibid.*, **265**, 62 (1951).

[6] F. Hund, *ibid.*, **273**, 312 (1953).

[7] L. Mazza and A. Iandelli, *Atti accad. liguie sci. e lettere*, **7**, 44 (1951); *Chem. Abstr.*, **47**, 4194*a* (1953).

[8] A. Zalkin and D. H. Templeton, *J. Am. Chem. Soc.*, **75**, 2453 (1953).

[9] D. H. Templeton and C. H. Dauben, *ibid.*, **76**, 5237 (1954).

[10] A. I. Popov and G. E. Knudsen, *ibid.*, **76**, 3921 (1954).

[11] N. C. Baenziger, J. R. Holden, G. E. Knudsen, and A. I. Popov, *ibid.*, **76**, 4734 (1954).

[12] K. S. Vorres and R. Riviello in "Rare Earth Research, Vol. III," Gordon and Breach, New York, N. Y., 1964, p 521.

[13] L. R. Batsonova and G. N. Kustova, *Russ. J. Inorg. Chem.*, **9**, 181 (1964).

[14] N. V. Podberegskaya, L. R. Batsonova, and L. S. Egorova, *J. Struct. Chem.* (U.S.S.R.), **6**, 815 (1965).

[15] D. J. M. Bevan, R. S. Cameron, A. W. Mann, G. Brauer, and U. Roether, *Inorg. Nucl. Chem. Letters*, **4**, 241 (1968).