SYNTHESIS AND SOME PROPERTIES OF BASIC CRYSTALLINE HAFNIUM DITUNGSTATE

S. S. Palitsyna, M. V. Mokhosoev, and V. I. Krivobok

UDC 542.91:546.786'832

According to a study of the hafnium tungstates in the HfO_2-WO_3 system, $HfOWO_4$ [1] and HfW_2O_8 [2] are formed. Basic crystalline zirconium tungstate has been obtained [3]. Taking into consideration the analogy in the properties of Zr and Hf, the problem in the present paper was to obtain basic crystalline hafnium tungstate and study its physicochemical properties.

EXPERIMENTAL

The starting solutions of 0.5 M hafnium oxychloride and 1.0 M Na_2WO_4 were prepared from cp $HfOCl_2 \cdot 8H_2O$ and analytical grade $Na_2WO_4 \cdot 2H_2O$. The reaction mixture was acidified with conc. HCl (d 1.18). The obtained sample was dried in the air and in a desiccator over calcined $CaCl_2$.

The air-dried sample (0.1-0.2 g) was dissolved in 30-40 ml of oxalic acid solution that had been saturated at ~20°C and then refluxed for a long time, and then the amount of HfO_2 was determined by precipitating the hafnium with cupferron [4]. The amount of WO_3 was determined photocolorimetrically using a 0.1-0.2 g sample, which was dissolved by long refluxing in a mixture of 6-7 g of NH_4HSO_4 and 20 ml of conc. H_2SO_4, while the amount of water was determined by the weight loss on ignition at 400°. Found: HfO_2 26.15; WO_3 61.02; H_2O 13.07%. $HfO_2 \cdot 2WO_3 \cdot 6H_2O$. Calculated: HfO_2 26.91; WO_3 60.00; H_2O 13.07%. The thermogram of the air-dried sample (derivatograph of the F. Paulik—J. Paulik—L. Erdey system, rate of raising the temperature = 10°/min) has three endothermic effects (106, 284, and 790°) and one exothermic effect (583°) on the heating curve. The curves for the weight loss of the sample show that the water present in the sample is removed in two steps, and mainly during the endothermic effects at 106 and 284°.

To ascertain the nature of the thermal effects and the resultant solid-phase transitions that take place here we employed the x-ray phase analysis data obtained for the powders, which were ignited at the corresponding temperatures. The x-ray patterns were taken on a DRON-1 diffractometer using Cu-filtered radiation.

DISCUSSION OF RESULTS

The air-dried hafnium tungstate sample is isostructural with zirconium molybdate and tungstate $Zr(OH)_2M_2O_7 \cdot 2H_2O$ (M = Mo, W) [5]. The parameters of the tetragonal cell are: a = 11.48, c = 12.41 Å (Table 1). This structure is also retained when the precipitate is heated at 200°, which indicates that hygroscopic water is present in the precipitate, and the former is removed at 106°. Further dehydration occurs when the precipitate is heated above 200°, and the structural water is removed (endothermic effect at 284°). As a result the tetragonal structure is destroyed and the x-ray pattern of this sample does not give any diffraction reflections. The crystalline structure is detected by x-ray when the sample is heated above 500°. A calculation of the powder pattern disclosed that the obtained phase crystallizes as a simple cubic lattice with a period of a = 9.12 Å (Table 2). An analogous structure is also characteristic for the HfW_2O_8 obtained by the ceramic method at 1200-1250° [2]. This makes it possible to state that hafnium tungstate HfW_2O_8 is formed after the final

Institute of Natural Sciences, Buryat Branch of the Siberian Section of the Academy of Sciences of the USSR, Ulan-Ude, and Donetsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 675-677, March, 1977. Original article submitted July 7, 1976.

TABLE 1. Indexing Data for Diffraction Pattern of $Hf(OH)_2$-$W_2O_7 \cdot 2H_2O$

I/I_1	d, Å	hkl	$10^2/d^2$ experiment	$10^2/d^2$ calculation	I/I_1	d, Å	hkl	$10^2/d^2$ experiment	$10^2/d^2$ calculation
50	5,79	0,20	2,99	3,00	40	2,47	332,224	1,68	1,69
10	4,88	112	4,12	4,11	20	2,36	242,134	1,77	1,75
60	4,20	022	5,63	5,63	15	2,10	152,044	2,25	2,24
50	3,63	130	7,58	7,58	25	1,95	026	2,63	2,63
100	3,12	132,004	1,03	1,02	25	1,90	060	2,76	2,75
15	2,86	040	1,22	1,21	15	1,87	352	2,86	2,84
20	2,73	024	1,34	1,34	30	1,80	136	3,00	3,00
25	2,61	042	1,47	1,47	25	1,73	262	3,32	3,30

TABLE 2. Indexing Results for Diffraction Pattern of HfW_2O_8

I/I_1	d, Å	hkl	$10^2/d^2$ experiment	$10^2/d^2$ calculation	I/I_1	d, Å	hkl	$10^2/d^2$ experiment	$10^2/d^2$ calculation
15	$5,2_7$	111	3,60	3,60	35	1,87	422	2,87	2,88
14	$4,5_5$	200	4,83	4,81	15	1,83	500,430	2,98	2,99
100	$4,0_9$	210	5,96	6,01	20	1,79	510,431	3,10	3,12
80	$3,7_4$	211	7,16	7,21	45	1,76	511,333	3,24	3,24
60	$3,2_2$	220	9,61	9,61	20	1,70	520,432	3,46	3,47
15	$3,0_4$	300,221	1,08	1,08	5	1,67	521	3,58	3,56
22	$2,8_0$	310	1,19	1,20	25	1,61	440	3,84	3,87
70	$2,7_5$	311	1,32	1,32	5	1,59	522,441	3,94	3,96
10	$2,6_4$	222	1,43	1,44	8	1,57	530,433	4,07	4,08
25	$2,5_4$	320	1,51	1,56	12	1,54	531	4,19	4,20
50	$2,4_5$	321	1,67	1,68	15	1,52	600,442	4,29	4,30
25	$2,2_2$	410,322	2,04	2,02	22	1,46	611,532	4,55	4,56
4	$2,1_0$	331	2,26	2,28	10	1,43	621,540,443	4,90	4,92
25	$2,0_4$	420	2,39	2,40	5	1,41	541	5,02	5,04
25	$1,9_9$	421	2,50	2,52	7	1,38	630,542	5,37	5,39
10	$1,9_5$	332	2,63	2,64	9	1,35	631	5,49	5,52

dehydration of the precipitate at 284°, which changes above 500° from the x-ray amorphous state to the crystalline state. The crystallization of HfW_2O_8 is accompanied by an exothermic effect at 583°. Anhydrous hafnium tungstate decomposes into the oxides HfO_2 and WO_3. The decomposition is accompanied by an endothermic effect at 790°. HfW_2O_8 and ZrW_2O_8 were obtained from the oxides at 1200-1250° [2]. Since ZrW_2O_8 was obtained from aqueous solution, with subsequent ignition at 300-500°, while HfW_2O_8 was obtained by ignition at 300-600°, we attempted to obtain HfW_2O_8 and ZrW_2O_8 also from a mixture of the oxides HfO_2 and WO_3, and ZrO_2 and WO_3, at 1100-1200°. Parallel with this, and at the same temperatures, we ignited the air-dried precipitates of zirconium and hafnium tungstates, which respectively decompose at 600-700 and 750-800° to the starting oxides. After holding for 4 h at 1100-1200° a portion of the samples was quenched in the air, while a second portion was cooled slowly along with the furnace. The x-ray studies disclosed that the samples, which were cooled slowly along with the furnace, contain a mixture of oxides, in which connection the amount of the samples decreased noticeably due to the sublimation of WO_3. The samples, which were quenched in the air at 1100-1200°, contained HfW_2O_8 and ZrW_2O_8 with a cubic structure, analogous to the samples that were obtained by precipitation from aqueous solution and subsequent ignition of the precipitates at 500-600°. The quenched samples, which were obtained from a mechanical mixture of the oxides together with HfW_2O_8 and ZrW_2O_8, also contained substantial amounts of still unreacted oxides HfO_2 and WO_3, and ZrO_2 and WO_3. The hafnium and zirconium tungstates, obtained by quenching at 1100-1200°, are stable up to 600-750° when heated in the air, while above this temperature they again decompose to a mixture of the oxides HfO_2 and WO_3, and ZrO_2 and WO_3. As a result, in the high-temperature synthesis from a mixture of the oxides it is possible to obtain HfW_2O_8 and ZrW_2O_8 only by quenching the samples from high temperatures, while the compounds HfW_2O_8 and ZrW_2O_8 decompose at 700°.

To explain the nature of the water, contained in $HfO_2 \cdot 2WO_3 \cdot 6H_2O$, we took the broad-band NMR spectra, which were decomposed using an atlas of the theoretical absorption curves of the water molecule [6]. The compound contains adsorbed water molecules with $R_{H-H} = 1.54$ Å and $\beta = 2.4$ Oe. A quantitative analysis of the spectra gives $n_{H^+} = 2$ and $n_{H_2O} = 5$ (Fig. 1).

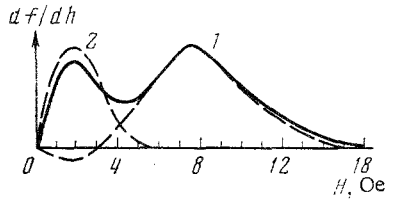

Fig. 1. NMR spectrum of $Hf(OH)_2W_2O_7 \cdot 2H_2O$: 1) experimental; 2) theoretical absorption curve.

Based on the chemical analysis and physicochemical study results, and also on the basis of the data given in [3], the air-dried $HfO_2 \cdot 2WO_3 \cdot 6H_2O$ sample obtained by us can be depicted as being $Hf(OH)_2W_2O_7 \cdot 2H_2O$ (three H_2O molecules are adsorbed).

CONCLUSIONS

1. Basic crystalline hafnium ditungstate $Hf(OH)_2W_2O_7 \cdot 2H_2O$ was obtained, which crystallizes as a tetragonal lattice. Ignition of the compound gave anhydrous hafnium tungstate with a cubic lattice, which is stable in the air up to 700-750°.

2. The anhydrous zirconium and hafnium ditungstates were obtained from the basic zirconium and hafnium tungstates, which are found in the metastable state at room temperature, and which decompose when heated to 700-750°.

LITERATURE CITED

1. V. I. Spitsyn, L. N. Komissarova, and Z. A. Vladimirova, Dokl. Akad. Nauk SSSR, 127, 120 (1959).
2. V. K. Trunov and L. M. Kovba, Zh. Neorg. Khim., 12, 3218 (1967).
3. A. Clearfield and R. Blessing, J. Inorg. Nucl. Chem., 36, 1174 (1974).
4. A. Ya. Sheskol'skaya, Zh. Anal. Khim., 17, 949 (1962).
5. A. Clearfield and R. Blessing, J. Inorgan. Nucl. Chem., 34, 2643 (1972).
6. R. N. Pletnev, Dissertation, Sverdlovsk (1969).