CHEMISTRY

Academician Vikt. I. SPITSYN, L. N. KOMISSAROVA, Z. A. VLADIMIROVA,

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician Vikt. I. SPITSYN, L. N. KOMISSAROVA, Z. A. VLADIMIROVA, Yu. P. SIMANOV, and N. N. TYUTYUEVA

ZIRCONIUM NIOBATE AND TANTALATE

The literature data on zirconium niobates are limited to the description of the compound $ZrO_2 \cdot 5Nb_2O_5$, which was obtained by the interaction of a solution of zirconium chloride and potassium niobate (^{1}), and also by fusing a mixture of ZrO_2 and Nb_2O_5 with NaF (^{2}). The individuality of this product was not confirmed by any physicochemical methods. Measurement of its specific gravity gave a value of 5.14 at 17-18°. Zirconium tantalates have not been described in the literature.

The present work is devoted to the study of the conditions for the formation of zirconium niobate and tantalate. Mixtures of zirconium and niobium hydroxides with different molecular ratios $ZrO_2 : Nb_2O_5$ (2 : 1, 1 : 1, and 1 : 2) were prepared. The initial hydroxides were preliminarily dried at 100°, thoroughly ground, and mixed. The resulting mixtures were sintered at 1300° in a silite furnace for a long time (40-60 hr). Along with the mixtures, separate hydroxides were calcined under the same conditions. X-ray diffraction patterns were taken for all the products obtained under identical conditions (with an iron anode in an RKD-57 camera). The X-ray patterns were measured on a comparator giving a reading accuracy of 0.05 mm. The line intensities were estimated visually on a five-point scale. The results of measuring the X-ray diffraction patterns of the calcined oxides were in good agreement with the literature data ($^{3-5}$). In the X-ray pattern of the mixture of ZrO_2 and Nb_2O_5 with an oxide ratio of 2 : 1, no lines characteristic of ZrO_2 and Nb_2O_5 were observed (Fig. 1), which indicates the formation of a new phase. In the X-ray patterns of other mixtures (1 : 1) and (1 : 2), in addition to the lines of the compound with an oxide ratio of 2 : 1, characteristic lines of Nb_2O_5 were observed. No new lines corresponding to compounds with another oxide ratio were observed.

Analogously to zirconium niobate, zirconium tantalate was synthesized under the same conditions by sintering a mixture of zirconium and tantalum hydroxides with a molecular ratio of ZrO_2 and Ta_2O_5 of 2 : 1. In the X-ray pattern of this mixture after sintering, no characteristic lines of ZrO_2 were found, although some lines may be attributed to free Ta_2O_5. However, the absence of three strong Ta_2O_5 lines, well indexed in a rhombic lattice with axes $a = 6.175 \pm 0.125$ kX, $b = 3.649 \pm 0.003$ kX, $c = 3.891 \pm 0.005$ kX (cf. the literature data (^{5})), makes it possible to conclude that this coincidence is purely accidental. Thus, in this case as well, the product of oxide sintering is a new phase. It should

Fig. 1. X-ray diffraction pattern diagram

Figure 1: Fig. 1. X-ray diffraction pattern diagram

be noted that the interaction of ZrO_2 with Nb_2O_5 proceeds much more readily than with Ta_2O_5. Formation of zirconium niobate is observed already upon heating the mixture to 1000° for 6 hr, whereas zirconium tantalate is formed only after prolonged holding of the mixture (40 hr) at 1300°.

In view of the negligible volatility of the initial oxides at the temperature of their interaction, the ratio $ZrO_2 : Nb_2O_5$ and $ZrO_2 : Ta_2O_5$ in the compounds obtained should not differ from the initial value and, evidently, corresponds to the formulas $2ZrO_2 \cdot R_2O_5$ or $(ZrO)_2R_2O_7$. The compounds obtained were analyzed for zirconium content as follows. A weighed portion of zirconium niobate was dissolved on heating in concentrated H_2SO_4; then, after dilution, zirconium phosphate was precipitated. Niobium was retained in solution by the addition of hydrogen peroxide. The precipitate of zirconium pyrophosphate was ignited at 900° and weighed. In the analysis of zirconium tantalate, the substance was decomposed by 2–3-fold evaporation with conc. HSO_4. The precipitate was treated with a 5% NaOH solution on boiling in order to convert the sulfates into hydroxides. Zirconium hydroxide dissolved in 2N HCl on heating, while tantalum remained completely in the precipitate. From the hydrochloric-acid solution, zirconium hydroxide was precipitated; it was ignited at 900° and weighed.

Fig. 1. X-ray diffraction pattern diagram

The analyses (average data from 2–3 experiments) showed the following ZrO_2 contents (in percent):

	Found	Calculated for $(ZrO)_2R_2O_7$
Zirconium niobate	49.40	48.11
Zirconium tantalate	36.20	35.80

Zirconium niobate and tantalate are white, finely crystalline compounds. The large number of lines (about 60) in the X-ray diffraction patterns of the compounds indicates low symmetry of the crystal lattice. The large values of the glancing angles are consistent with the small density values: 5.70 for $(ZrO)_2Nb_2O_7$ and 7.82 for $(ZrO)_2Ta_2O_7$. (The specific gravities were determined pycnometrically at 25°.)

To confirm the individual character of the compounds obtained and to compare their properties, the melting temperatures were determined, the thermal stability and behavior toward certain chemical reagents were investigated. The melting of zirconium niobate and tantalate was carried out in a high-frequency furnace for vacuum and open melting of the MVIT-3 type. The temperature was measured with an "Opir-09" optical pyrometer. Melting of the substance was observed visually. As a result of the experiments carried out, it was established that the melting temperatures of zirconium niobate and tantalate are $1700 \pm 20^\circ$ and $1730 \pm 20^\circ$, respectively. According to X-ray phase analysis, both compounds melt without decomposition and, in the temperature range 20—1400°, undergo no phase transformations. The latter was confirmed by studying the thermal stability of the compounds with the use of a Kurnakov pyrometer. Heating thermograms of $(ZrO)_2Nb_2O_7$ and $(ZrO)_2Ta_2O_7$ are presented in Fig. 2.

Fig. 2. Thermograms. A $-(ZrO)_2Nb_2O_7$ (average heating rate 10°/min), $-$ $(ZrO)_2Ta_2O_7$ (average heating rate 8°/min).

The rate of interaction of zirconium niobate and tantalate with CCl_4 vapors was studied. For comparison, under the same conditions the corresponding mixtures of ZrO_2 with Nb_2O_5 (2 : 1) and ZrO_2 with Ta_2O_5 (2 : 1) were chlorinated. The conditions for carrying out the experiments differed only in the rate of supply of CCl_4 and in the surface dimensions of the preparations taken. Carbon tetrachloride was fed into the reaction quartz tube by a stream of air, which was passed at a constant rate through a bottle filled with CCl_4. Chlorination was carried out in the temperature range 500—650° for 30 min. After the experiment, the residue was weighed and, in some cases, its ZrO_2 content was determined. In addition, X-ray phase analysis of the residue was carried out. The results obtained, representing average values from 3–4 determinations, are given in Table 1.

Table 1

Chlorination of zirconium niobate and tantalate and of mixtures of the initial oxides (2 : 1) with carbon tetrachloride. Charge 0.2 g, grain size $< 100\,\mu$, chlorination duration 30 min.

Series of experiments	Feed rate of CCl_4, $g/cm^2 \cdot h$	Substance	Weight loss, %, at 500°	Weight loss, %, at 550°	Weight loss, %, at 600°	Weight loss, %, at 650°
1	0.05	$(ZrO)_2Nb_2O_7$	2.3	5.4	6.6	
1	0.05	Mixture ZrO_2 and Nb_2O_5 (2 : 1)	7.1	14.9	24.3	
2	0.12	$(ZrO)_2Ta_2O_7$	–		4.8	6.9

Series of experiments	Feed rate of CCl_4, $g/cm^2 \cdot h$	Substance	Weight loss, %, at 500°	Weight loss, %, at 550°	Weight loss, %, at 600°	Weight loss, %, at 650°
2	0.12	Mixture ZrO_2 and Ta_2O_5 (2 : 1)	–		16.5	31.8
3	0.10	$(ZrO)_2Nb_2O_7$	4.9	11.7	14.4	
3	0.10	$(ZrO)_2Ta_2O_7$	–	2.5	4.0	

It should be noted that zirconium niobate and tantalate are chlorinated 3-4 times more slowly than the corresponding mixtures of oxides. Zirconium tantalate is more resistant to the chlorinating agent: at 500°, in contrast to zirconium niobate, the tantalate is not chlorinated at all. According to chemical and X-ray phase analyses, the principal amount of zirconium niobate and tantalate is not altered in the course of chlorination.

To characterize the stability of zirconium niobate and tantalate toward solutions of various reagents, the action was tested

HCl (36%), H_2F_2 (25%), H_2SO_4 (94%), and NaOH (40%). A weighed portion of the substance (0.1 g) was treated with 50 ml of reagent for 4 h at 85-90°. The residue was washed with water, dried at 100°, weighed, and subjected to X-ray phase analysis. It was established that both compounds studied possess high stability with respect to the reagents tested (Table 2).

Table 2

Relation of zirconium niobate and tantalate to reagents. Weighed portion 0.1 g, temperature 85-90°, treatment time 4 hours

Reagent	Amount of dissolved substance, g/100 ml of reagent	Amount of dissolved substance, g/100 ml of reagent
	$(ZrO)_2Nb_2O_7$	$(ZrO)_2Ta_2O_7$
HCl, 36%	0.0320	0.0000
H_2SO_4, 94%	0.0920	0.0000
H_2F_2, 25%	0.1008	0.0610
NaOH, 40%	0.0266	0.0082

The best solvent for them is a concentrated solution of H_2F_2. Zirconium tantalate is characterized by greater stability in comparison with the niobate. In contrast to the latter, zirconium tantalate is practically insoluble in hot solutions of conc. HCl and H_2SO_4, in mixtures of ammonium sulfate with sulfuric acid, and does not fuse with sodium pyrosulfate, K_2CO_3, or sodium peroxide. Whereas zirconium niobate dissolves readily on heating to 220° in conc. H_2SO_4, decomposition of zirconium tantalate occurs only as a result of evaporating the substance with conc. H_2SO_4. Under the action of the above-mentioned reagents, the undissolved portion of the compounds, according to X-ray phase analysis, undergoes no changes. Thus, zirconium niobate and tantalate exhibit considerable chemical stability.

Moscow State University
named after M. V. Lomonosov

Received
22 XII 1959

CITED LITERATURE

[1] A. Larsson, Zs. anorg. Chem., 12, 188 (1896).
[2] P. J. Holmquist, Zs. anorg. Chem., 18, 84 (1898).
[3] C. E. Curtis, L. M. Doney, Z. R. Johnson, J. Am. Ceram. Soc., 37, 458 (1954).
[4] G. Brauer, Zs. anorg. Chem., 248, 1 (1941).
[5] P. A. Sellers, S. Fried et al., J. Am. Chem. Soc., 76, 5935 (1954).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.