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## Abstract

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# X-RAY DIFFRACTION STUDY OF ZIRCONIUM AND HAFNIUM DIOXIDES AT TEMPERATURES UP TO 2750°

*(Presented by Academician V. A. Kirillin, August 10, 1964)*

Zirconium and hafnium dioxides, with melting temperatures of 2700 and 2800°, are promising materials for high-temperature technology.

However, considerable complications in the practical use of $ZrO_{2}$ and $HfO_{2}$ are associated with the reversible polymorphic transformations that occur in them upon heating. A significant number of works have been devoted to questions of stabilizing oxides in the cubic or tetragonal form. One of the possible mechanisms for stabilizing zirconium dioxide in the cubic form is considered, for example, in work ($^{1}$). The starting premises in this case were the well-known considerations of Goldschmidt, Magnus, and Pauling concerning crystal-chemical criteria determining the limits of stability of crystal structures with rutile- and fluorite-type lattices. According to these ideas, the fluorite lattice for $ZrO_{2}$ could be stable only at a ratio $R_k / R_a \geq 0.732$. Since in reality for $ZrO_{2}$ $R_k / R_a = 0.66$ ($^{2}$), the authors of the cited work ($^{1}$) directly relate the mechanism of stabilization of the cubic lattice to the necessity of increasing the distance between anion positions. Such a mechanism is well justified qualitatively for the known examples of stabilization of cubic $ZrO_{2}$ by replacing part of the cations with isovalent metal ions of larger radius, or with ions of lower valence.

Proceeding from these considerations, one may also expect that expansion of the lattice upon heating, for pure $ZrO_{2}$, may lead at sufficiently high temperatures to the attainment of the stability region of the cubic modification. It is not difficult to estimate qualitatively that, for the ionic radii $Zr^{4+}$ and $O^{2-}$, the distance between anion positions required to ensure stability of the cubic lattice is achieved with an average increase in the lattice parameters (due to heating) of approximately 4%.

In essence, as Weber showed in a detailed review ($^{3}$), the literature contains no direct confirmations of the existence of a high-temperature cubic modification of zirconium dioxide, with the exception of a brief report by Smith and Cline, published in 1962 ($^{4}$). The results of this latter work, performed by the X-ray diffraction method, were called into question by Weber in connection with

Fig. 1. Schematic diagram of a high-temperature diffractometric X-ray chamber. 1 —specimen with cassette, 2 —radiative tungsten heater, 3 —electron gun for heating the specimen to temperatures above 2000°

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possible stoichiometric disturbances in the sample upon heating to temperatures of about 2400° in vacuum.

A direct test of the possibility of the existence of a cubic form for pure zirconium dioxide at high temperatures, and also for the close analogue of `ZrO$_{2}$`—hafnium dioxide—therefore appeared to be of great interest. There are no indications at all in the literature concerning the existence of a cubic modification for pure hafnium dioxide.

It is known only from ASTM data that the transition from the monoclinic to the tetragonal form occurs, apparently, at temperatures above 1800°.

X-ray studies of the polymorphism of zirconium and hafnium dioxides were carried out in a high-temperature X-ray chamber designed and built by us and mounted on a URS-50-IM ionization diffractometer (Fig. 1). The basic arrangement of the chamber is as follows: the specimen to be X-rayed is pressed into a molybdenum cassette **1**; heating to temperatures of ~2000° is accomplished by means of a radiative tungsten heater **2**, and to higher temperatures by means of an electron gun **3** located on the front side. High-temperature exposures are made in a vacuum of the order of $5 \cdot 10^{-6}$ mm Hg.

**Fig. 1.** Schematic diagram of a high-temperature diffractometric X-ray chamber. **1** —specimen with cassette, **2** —radiative tungsten heater, **3** —electron gun for heating the specimen to temperatures above 2000°.

When the specimen is heated with the electron gun, its outer surface has the highest temperature. Owing to this, the possibility of contamination of the specimen associated with evaporation of other heated parts of the fixture is largely eliminated.

Specimens of $ZrO_2$ and $HfO_2$ with an impurity content of not more than 0.2% were investigated. In addition to anhydrous zirconium dioxide preparations, preliminarily synthesized zirconium hydroxide was also used for preparing specimens. Slow decomposition of the hydroxide at a temperature of about 400°, in agreement with the data of works ($^5$) and ($^6$), led to the formation of the so-called low-temperature cubic, and with a further increase in temperature, to the "low-temperature tetragonal modification." The nature of the stabilization of these low-temperature "modifications" remains as yet unclear. At a temperature of about 700–800° the low-temperature tetragonal modification irreversibly transformed into the stable monoclinic form. The lattice parameters of the observed modifications are given in Fig. 2. Upon heating anhydrous zirconium dioxide, the reversible polymorphic transformation monoclinic ⇄ tetragonal was observed in the temperature interval 1100-1200°. Subsequent heating to a temperature of about 2300° made it possible to detect a second polymorphic transformation, tetragonal ⇄ cubic. A complete X-ray pattern of the high-temperature cubic form of $ZrO_2$, obtained at 2330°, is shown in Fig. 3. The corresponding interplanar spacings and intensities of the diffraction lines are given in Table 1.

Thus, the recorded high-temperature cubic form of zirconium dioxide has a fluorite-type lattice with parameter $a = 5.256 \pm 0.003$ Å at 2330°. By repeated heating and cooling within the range 2200—2350°, it was established that the observed

Fig. 2 Fig. 3

**Fig. 2.** Dependence of the parameters of the tetragonal and cubic lattices on temperature for pure zirconium and hafnium dioxides.
1 –$ZrO_2$ –low-temperature cubic modification; 2 –$ZrO_2$ –high-temperature cubic modification; 3 –$ZrO_2$ –low-temperature tetragonal; 4 –$ZrO_2$ –tetragonal (heating); 5 –$ZrO_2$ –tetragonal (cooling after heating to 2350°); 6 –$HfO_2$ –tetragonal; 7 –$HfO_2$ –cubic.

**Fig. 3.** X-ray pattern of pure zirconium dioxide obtained at 2330° (cubic modification)

transformation is completely reversible, and the temperature hysteresis of the transformation does not exceed 20—30°. It should be mentioned that the temperature hysteresis of the monoclinic ⇄ tetragonal transformation is 100—150°.

Upon cooling the specimen from the indicated highest experimental temperatures, repeated exposures were made for a number of temperatures in the region of existence of the tetragonal and monoclinic modifications. In all cases the parameter values at the corresponding temperatures remain constant (Fig. 2).

**Table 1**

| *d*, Å (measured) | *I* (relative units) | *hkl* | *d*, Å (calculated) |
|---:|---:|:---:|---:|
| 3.037 | 69 | (111) | 3.035 |
| 2.629 | 100 | (002) | 2.628 |
| 1.858 | 62 | (202) | 1.859 |
| 1.583 | 51 | (113) | 1.585 |
| 1.517 | 4 | (222) | 1.517 |

Stable reproduction of the transition temperatures under repeated heating and cooling, as well as constancy of the parameters for the monoclinic and tetragonal forms, give grounds to believe that, upon heating $ZrO_2$ in vacuum to temperatures of the order of 2400°, no substantial disturbance of the stoichiometry of the oxide lattice occurs.

As is seen from the graph shown in Fig. 2, the stabilized tetragonal modification of $ZrO_2$, formed during decomposition of the hydroxide at a temperature of $\sim 500°$, has a lattice-parameter value in good agreement with the extrapolated values obtained for the stable tetragonal modification in the temperature range from 1200 to 2300°.

On the other hand, if one conditionally assumes that the temperature dependence of the cubic-lattice parameter has the same slope as for the parameters $c$ and $a$ of the tetragonal lattice, then, as is seen from the graph, the value

the parameter for the metastable cubic and the high-temperature cubic forms is also in fairly good agreement.

The high-temperature diffraction patterns obtained for hafnium dioxide made it possible to establish the presence of a reversible polymorphic transformation, monoclinic tetragonal, in the temperature interval 1900–2000°. A second transformation, analogous to the tetragonal cubic transformation of $ZrO_2$, could be recorded only at very high temperatures close to the melting temperatures of $HfO_2$. In this case the temperature was estimated from the power dissipated on the specimen by the electron beam, and according to this estimate was 2700–2750°. Examination of the specimen after the diffraction run showed that at the indicated temperatures, despite the relatively short duration of the run ($\sim 30$ min), intensive sublimation of hafnium dioxide had occurred. The surface of the specimen, as in the experiments with zirconium dioxide, showed no noticeable contamination.

The presence of the transformation was indicated by replacement of the doublet of the (200) and (002) lines by the (200) line of the cubic modification.

The tetragonal cubic transformation for hafnium dioxide is likewise reversible. The lattice parameter of the cubic modification at 2750° is $\sim 5.300 \pm 0.010$ Å.

Thus, for pure zirconium and hafnium dioxides the truly stable crystalline modifications are: monoclinic—in the temperature range from room temperature to 1150° for $ZrO_2$ and to 1950° for $HfO_2$; tetragonal—from 1150 and 1950° to 2300 and 2700°, respectively; and face-centered cubic—from 2300° for $ZrO_2$ and 2700° for $HfO_2$ up to the melting temperatures.

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# REFERENCES

1. I. I. Vishnevskii, A. G. Garvish, B. Ya. Sukharevskii, *Collection of Scientific Papers of the Ukrainian Scientific-Research Institute of Refractories*, issue 6 (3), 1962, p. 74.

2. L. Pauling, *The Nature of the Chemical Bond*, 1948.

3. B. C. Weber, *J. Am. Ceram. Soc.*, **45**, No. 12, 614 (1962).

4. D. K. Smith, C. F. Cline, *J. Am. Ceram. Soc.*, **45**, No. 5, 249 (1962).

5. Faintly Fay Kan, A. K. Kuznetsov, E. K. Keier, *Izv. AN SSSR, OKhN*, 1964, No. 6, 956.

6. L. N. Komissarova, Yu. P. Simanov, Z. A. Vladimirova, *ZhNKh*, **5**, issue 7, 1413 (1960).

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