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The crystal structure of tetragonal ZrO_2.

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The high temperature, tetragonal form of ZrO_2 was first observed by Ruff & Ebert (1929) during their studies of polymorphism in ZrO_2 and the stabilization of zirconia. Since that time it has been generally assumed that the tetragonal form represents a slightly distorted CaF_2 type structure. To preserve a convenient analogy to the face-centered CaF_2 structure, the lattice constants and indices of tetragonal ZrO_2 have often been described in terms of a face-centered tetragonal lattice, rather than the more conventional body-centered lattice which was presumably appropriate for the ZrO_2 phase. In this note, the conventional descriptions of tetragonal phases will be utilized.

In the course of a high-temperature X-ray diffraction study of tetragonal ZrO_2, a number of previously unreported reflections, which are inconsistent with a body-centered lattice, have been observed. The intensities of most of these reflections are rather low, but the strongest of these (the (102) reflection) was observed throughout the temperature range from 1200 to 1950 °C. during heating and from 1950 to 900 °C. during cooling, both in purified ZrO_2 as well as in specimens containing about 2% of hafnium.

The X-ray analysis was made with a General Electric XRD-5 unit using Cu and Cr $K\alpha$ radiations in conjunction with a proportional counter as radiation detector. Various ZrO_2 samples were heated up to 1350 °C. in a high-temperature furnace made by TEM-PRES INC., State College, Pennsylvania, while the high temperature-high vacuum attachment made by Materials Research Corporation, Yonkers, New York, was used for temperatures up to 1950 °C.

All reflections from hafnium-free ZrO_2 specimens were indexed on the basis of a primitive tetragonal lattice with

$$a = 3{\cdot}64,\ c = 5{\cdot}27\ \text{Å}\ \text{(at 1250 °C.)},$$
$$\text{Space group } D_{4h}^{15}\text{–}P4_2/nmc.$$

There are two molecules in the elementary cell. With the origin at $\bar{4}m2$ the zirconium and oxygen atoms are located in positions similar to those in a CaF_2 type structure in:

2 Zr (*a*) 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;
4 O (*d*) $0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$; $0, \frac{1}{2}, \frac{1}{2}+z$; $\frac{1}{2}, 0, \frac{1}{2}-z$.

The variable-position parameter for oxygen and the isotropic thermal motions of the zirconium and oxygen atoms were determined by least squares analysis of the powder diffraction data to be:

$z_O = 0{\cdot}185$,
$B_{Zr} = 1{\cdot}66$ and $B_O = 3{\cdot}11$ Å^2 (at 1250 °C.).

A comparison of observed and calculated structure factors is shown in Table 1. The low discrepancy factor of 6·7% may be attributed in part to the small number of variables in this structure and, in part, to the predominance of the scattering of the zirconium atoms in special positions over that of the oxygen atoms in composing the structure factors. When the oxygen atoms are placed in $z = \frac{1}{4}$, as in the CaF_2 structure type, the discrepancy factor rises to 9·4%, indicating that such a structure is improbable.

Table 1. *Comparison of observed and calculated structure factors for tetragonal* ZrO_2

hkl	F_o	F_c	*hkl*	F_o	F_c
101	28·9	30·7	303	14·9	13·1
002	20·9	21·9	321	14·9	13·0
110	20·0	18·3	322	0	1·2
102	6·4	6·5	224	12·6	11·5
112	29·6	29·7	400	15·8	12·8
200	31·8	31·7	304	0	−1·4
103	21·9	22·2	215	11·0	10·8
211	22·7	21·8	006	12·2	11·7
202	17·8	17·7	323	11·3	10·6
212	4·0	3·2	411	11·2	10·5
004	19·3	18·5	314	11·1	10·5
220	22·1	21·9	402	8·3	9·4
104	3·5	−3·4	330	8·2	8·9
213	16·0	16·7	106	0	0·8
301	16·5	16·5	412	0	0·9
114	16·1	16·6	116	8·1	8·7
222	13·6	14·1	332	11·4	10·0
310	13·6	13·1	420	11·3	10·3
302	0	1·9	324	0	−1·0
204	14·3	14·3	305	8·3	8·8
312	16·6	15·7	206	9·6	9·5
214	0	−2·1	413	9·3	8·7
105	13·8	13·4	422	7·4	7·8

In tetragonal ZrO_2 each zirconium atom is surrounded by eight oxygen atoms, four at a distance of 2·065 Å in a flattened tetrahedron and four at 2·455 Å in an elongated tetrahedron which is rotated 90° relative to the former one. Each oxygen atom has two oxygen neighbors at 2·635 Å and four at 2·655 Å, and is bonded to two zirconium atoms at 2·065 Å, while two more Zr atoms are 2·455 Å away. This combination of two distorted tetrahedra is similar to zirconium silicate where Krstanović (1958) measured Zr-(4)O = 2·15 and Zr-(4)O = 2·29 Å. Furthermore, tetragonal ZrO_2 is isostructural with red HgI_2.

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References

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