

X-Ray Study on Solid Solutions of Oxygen in Hafnium

T O R E D A G E R H A M N

*Institute of Inorganic and Physical Chemistry,
University of Stockholm, Stockholm, Sweden*

In connection with studies on the titanium-oxygen and zirconium-oxygen systems which are being conducted at this Institute, an investigation has been made of the solubility of oxygen in the hexagonal close-packed modification of hafnium.

Hafnium metal (Imperial Chemical Industries Ltd., crystal bar, Hf min. 98.5 % with Zr 1.0–1.5 % and O 400 ppm as major impurities) and hafnium dioxide obtained by heating the metal in a stream of oxygen were used to prepare several samples within the composition range $\text{HfO}_{0-0.5}$. Mixtures of the starting materials were arc-melted in an argon atmosphere and then heat-treated in evacuated silica capsules for one month at 600°C followed by quenching in water. X-Ray powder photographs were taken in a Guinier focusing camera using $\text{CuK}\alpha_1$ radiation. Details of the methods used in the preparative and X-ray work have been given in previous articles^{1,2}.

The results of the investigation are summarized in Table 1 and Fig. 1. The introduction of oxygen in solid solution increases the hafnium lattice parameters a and c over the entire range of solubility. The axial ratio c/a , however, is practically constant after a slight rise at low oxygen contents. The limit of solubility was found to be at 20.6 at. % ($\text{HfO}_{0.26}$). Samples with higher oxygen contents contain dioxide as the additional phase.

Table 1. Unit-cell parameters for samples HfO_x heat-treated at 600°C for 1 month.

x	a (Å)	c (Å)	c/a
0.00	3.1969	5.0604	1.5829
0.10	3.2044	5.0830	1.5863
0.15	3.2072	5.0889	1.5867
0.20	3.2112	5.0942	1.5864
0.25	3.2142	5.0983	1.5862
0.30	3.2148	5.1006	1.5866 (two-phase region)
0.35	3.2145	5.0990	» » »
0.40	3.2150	5.0990	1.5860 » » »
0.50	3.2147	5.1003	1.5866 » » »

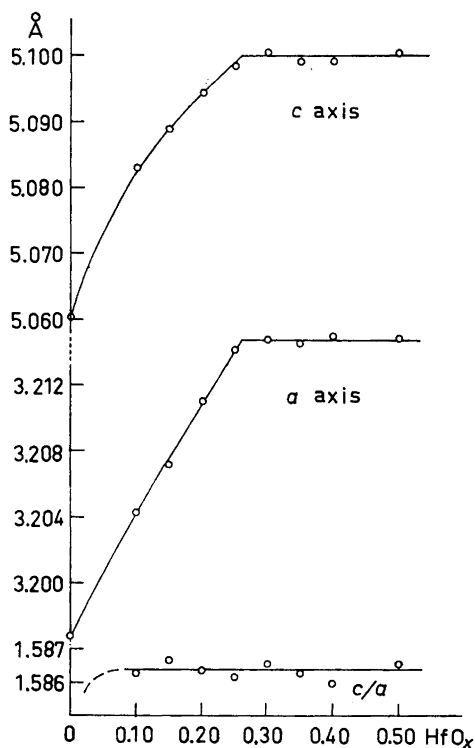


Fig. 1. Unit-cell parameters for samples HfO_x heat-treated at 600°C for 1 month.

As is the case for the titanium-oxygen and zirconium-oxygen solid solutions, the oxygen atoms dissolved in hafnium must occupy interstitial positions in the metal structure. The powder photographs of the specimens HfO_x did not show any extra lines which indicates that the distribution of the interstitial atoms is a random one at all concentrations of oxygen.

A comparison with the titanium-oxygen¹ and zirconium-oxygen³ systems indicates a decrease in the solubility limit in the order $\text{TiO}_{0.50}$, $\text{ZrO}_{0.40}$ and $\text{HfO}_{0.26}$. The appearance of ordered arrangements of the interstitial oxygen atoms and the peculiar shape of the lattice parameter curves observed for the former two systems entirely lack a counterpart in the solid solutions of oxygen in hafnium.

The author wishes to express his gratitude to Dr. Arne Magnéli and Fil.kand. Bo Holmberg for their kind interest in this investigation which was undertaken in connection with research programmes financially supported by the *Swedish Natural Science Research Council* and by the *AB Atomenergi Ltd.*

1. Andersson, S., Collén, B., Kuylenstierna, U. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1641.
2. Westman, S. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1587.
3. Holmberg, B. and Dagerhamn, T. *To be published in Acta Chem. Scand.*

Received December 17, 1960.

On Light-Induced Phosphorylation and Oxidation of Reduced Diphosphopyridine Nucleotide in *Rhodospirillum rubrum*

MARGARETA BALTSCHIEFFSKY

Wenner-Gren Institute, University of Stockholm, Sweden

The highest values yet reported for the specific activity of bacterial light-induced phosphorylation, have been obtained with isolated chromatophores from the photosynthetic bacterium *Rhodospirillum rubrum*, which has been ground with alumina (Alcoa A-301) in order to rupture the intact cells¹. During the last year we have also used sand (Baker, purified) as an abrasive instead of alumina, and these preparations have usually shown a higher photophosphorylating activity when compared to alumina-ground preparations from the same batch of bacteria. However, the yield has been considerably lower. The reduced diphosphopyridine nucleotide oxidase (DPNH-oxidase) activity in "sand-preparations" and "alumina-preparations" has also been investigated. Its distribution between various fractions depends on the method of preparation. The DPNH-oxidase has been partly purified.

Acta Chem. Scand. **15** (1961) No. 1

Table 1. Comparison of light-induced phosphorylation in preparations made with sand and with alumina. The values are given as μ moles orthophosphate esterified per hour per mg chlorophyll. Phosphorylation was determined as in Ref.² The 25 000 *g* fraction was used.

Batch	Alumina	Sand
1	320	480
2	280	530
3	420	540
4	620	490
5	230	530

The cells were grown, harvested and ground with alumina according to previously described methods². When sand grinding was employed the procedure was as follows: the paste of wet bacteria was weighed and transferred to an ice-cold mortar. Cold sand in an amount equivalent to twice the weight of the bacteria was added, the mixture was ground for 3 min and subsequently extracted with ice-cold 0.2 M glycylglycine buffer, pH 7.4, 2 ml for each gram of bacteria. The extracted material was centrifuged 10 min at 10 000 *g*, the sediment discarded and the supernatant centrifuged 1 h at 25 000 *g* or 40 000 *g*. The latter force brings down all or almost all the colored material in contrast to its effect on "alumina preparations" where more than one third of the colored material normally remains in the supernatant. This indicates that "sand preparations" contain larger particles, presumably more "intact" chromatophores.

Table 2. Typical distributions of DPNH-oxidase activity in preparations from two batches of *Rhodospirillum rubrum*. The activity was measured at 340 $m\mu$ in a Beckman DK2 spectrophotometer. The values are given as μ M (μ moles per liter) DPNH oxidized per min per mg protein. The initial concentration of DPNH was 10^{-4} M.

Batch	Abrasive	Fraction		
		25 000 <i>g</i>	100 000 <i>g</i>	Supernatant
5	Alumina	2.6	5.5	7.3
5	Sand	5.8	13.3	1.8
8	Alumina	10.0	4.3	11.1
8	Sand	21.0	3.3	2.2