

Crystal structure of synthetic hafnon, HfSiO_4 , comparison with zircon and the actinide orthosilicates

J. ALEXANDER SPEER AND BRIAN J. COOPER

*Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061*

Abstract

A crystal structure refinement of a synthetic hafnon, HfSiO_4 , space group $I4_1/amd$ with $a = 6.5725(7)\text{\AA}$, $c = 5.9632(4)\text{\AA}$, $Z = 4$, $D = 6.97\text{ gm cm}^{-3}$, produced positional parameters for oxygen of $y = 0.0655(13)$ and $z = 0.1948(14)$ at $R = 0.054$. Hafnon has a zircon structure and the similar ionic radii of Hf (0.83\AA) and Zr (0.84\AA) accounts for the interatomic distances and angles of hafnon and zircon being identical within the stated errors, although hafnon has systematically smaller distances and corresponds to a zircon at 29.5 kbar pressure. Combining the hafnon, zircon and thorite structure refinements allows prediction of the oxygen positional parameters and bond lengths for the actinide (Pa, U, Np, Pu and Am) orthosilicates as well as possible extent of the solid solution among these zircon-structure silicates.

Introduction

The most common compositional substitution for Zr in zircon is Hf (see Speer, 1980a for discussion and references). Most natural zircons have a Zr:Hf ratio of 40:1, which corresponds to their crustal abundance ratio. Synthetic HfSiO_4 is isostructural with zircon and was called hafnon by Curtis *et al.* (1954), a name eventually approved for the rare, natural end member by the International Mineralogical Association. Hafnon is found in pegmatites with Ta and Nb minerals, in particular where there is enrichment in the pegmatite of the even-odd pair ^{72}Hf – ^{73}Ta over the ^{40}Zr – ^{41}Nb pair.

Hf and Zr are extremely similar in their chemical properties; Hf was distinguished from Zr only in 1922. This similarity is a result of the similarity in their electronic structures and ionic radii which permits complete miscibility in most Zr–Hf compounds. While there is little change in the geometry and dimensions of these structures with chemistry, there are greater changes in some physical properties (*e.g.*, density and thermal neutron capture cross section). Zirconium has a cross section of 0.18 barn whereas Hf has a larger value of 115 barn. The presence of Hf in zircon increases its susceptibility to metamictization, and Hf compositional zoning causes a nonuniform susceptibility. Hf-rich zones in natural zircons are usually more metamict, contain

greater compositional substitutions for Zr and Si and yield discordant ages (see Speer, 1980a, chemical zoning). A crystal structure refinement of hafnon was performed to determine if any geometrical or dimensional differences accompany the physical property differences between hafnon and zircon. The comparison of the hafnon structure with that of zircon and thorite permits an understanding of the crystal chemistry of the solid solutions among hafnon, zircon and the actinide orthosilicates.

Experimental

Hafnon crystals were grown in a platinum crucible from a Li_2MoO_4 melt which was about 5 percent by weight HfO_2SiO_2 . The starting material was spectroscopic grade, 99.99% HfO_2 from Apache Chemicals, Inc. and Puratronic SiO_2 from Johnson Matthey Chemicals, Ltd. The crucible was held at 1000°C for four days in an air-atmosphere muffle furnace. The crystals were separated from the quenched flux in hot water.

The crystals were tetragonal dipyramids, and wavelength dispersive electron microprobe scans of the crystals detected only Hf and Si. The space group of hafnon, determined by precession method, is $I4_1/amd$. Unit-cell parameters were obtained by least-squares refinement of 20 automatically-centered reflections in the 2θ range of 74 to 93° (Table 1). Data were collected on a crystal $0.12 \times 0.14 \times$

Table 1. Crystallographic data, positional and thermal parameters for synthetic hafnon, HfSiO₄

Space group: $I 4_1/amd$				
Unit-cell parameters:				
	this study	D	SH	RGS
a, Å	6.5725(7) ¹	6.581	6.573	6.569
c, Å	5.9632(4)	5.967	5.964	5.967
V, Å ³	257.6	258.4	258.1	257.5
ρ, gm cm ⁻³	6.97	6.95	6.97	6.98
μ	403.8 cm ⁻¹ (MoK _α) ²			
Positional and thermal parameters:				
Atom	x	y	z	B
Zr ³	0.0	0.75	0.125	0.0035(1) 0.0034(2)
Si	0.0	0.75	0.625	0.05(8)
O	0.0	0.0655(13)	0.1948(14)	0.73(7)

¹Parenthesized figures represent esd's of last units cited.

²Mass attenuation coefficients are from International Tables for X-ray Crystallography, Vol. 4.

³Zr is in site a with site symmetry $4_2 m$.

$\beta_{11} = \beta_{22}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$

References: D, Durif (1961); SH, Salt and Hornung (1967);

RGS, Ramakrishnan *et al.* (1969).

0.22 mm in size, mounted with [110] parallel to the phi axis of an automated Picker four-circle diffractometer. Intensity measurements were made with Nb-filtered MoK α radiation using the constant precision intensity technique of the Krisel X-ray diffractometer control system (Finger and Hadidiacos, 1981). All 1386 reflections in one octant of reciprocal space from 3° to 95° 2 θ were collected. Three reference reflections were monitored every two hours. The intensity sums of these reflections varied less than 4 percent from the average. The data were corrected for Lorentz, polarization and absorption effects and then were symmetry averaged to produce 203 reflections with intensities greater than 2 σ .¹ Because the crystal is a highly modified tetragonal prism, absorption corrections were made assuming an ellipsoidal shape. Maximum and minimum transmission coefficients were 0.066 and 0.028 respectively. The refinement was accomplished using the neutral atom scattering factors of Doyle and Turner (1968) and coefficients for anomalous scat-

tering of Cromer and Libermann (1970). Hf is located at (0, 3/4, 1/8), Si at (9, 3/4, 5/8) and O at (0, y, z). Initial atomic coordinates and isotropic temperature factors were those of a zircon refinement by Hazen and Finger (1979). Because of the high correlation among most of the parameters, the refinement was done in parts. The scale factor and isotropic temperature factor for Hf were each refined separately. The R-factor, $R = (|F_o| - |F_c|)/|F_o|$, decreased from 0.239 to 0.091. The silicon isotropic temperature factor and oxygen positional parameters and isotropic temperature factor were next varied simultaneously, keeping the scale factor and Hf temperature factor fixed, reducing R to 0.089. Finally, the isotropic temperature factor for Hf was converted to anisotropic temperature factors, all parameters were permitted to vary, and an isotropic extinction correction was made. The final $R = 0.054$ and $G = 0.96$. Table 2² lists observed and calculated structure amplitudes.

Results

Refined structural parameters for hafnon are presented in Table 1 and selected interatomic distances and angles are listed in Table 3. Orientation and magnitude of the hafnium thermal ellipsoid are included in Table 3. Descriptions of the zircon structural type are given by Speer (1980a) or Robinson *et al.* (1971). The isotropic temperature factor for silicon is small. Determination of light-atom parameters in a structure with heavy atoms is difficult by X-ray methods and at best leads to large uncertainties in the refined parameters. In hafnon, the silicon makes the smallest contribution to the structure factors and the only variable parameter is its temperature factor. Temperature factors are sensitive to absorption corrections, but the difficulty with the silicon temperature factor is believed to result from its high correlation with the scale factor, Hf β_{11} and Hf β_{33} . The correlation coefficients are 0.34, 0.78 and 0.60 respectively. These three parameters are also highly correlated (>0.60 among themselves). Perhaps the greatest error in the silicon temperature factor lies in its optimistically small *esd*. A complete list of correlation factors is included in Table 2.

¹Programs utilized for data handling, refinement and geometry calculations were local modifications of DATALIB, DATASORT, ORXFLS3 and ORFFE3. These programs are included in the *World List of Crystallographic Computer Programs (3rd ed. and supplements)*.

²To obtain a copy of this table, order Document Am-82-205 from the Mineralogical Society of America, Business Office, 2000 Florida Avenue, NW, Washington, DC 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Selected interatomic distances and angles for synthetic hafnon

Si tetrahedron distances (Å) and angles (°)		
Si-O	[4]*	1.620(8)**
O-O†	[2]	2.425(16)
O-O	[4]	2.749(15)
O-Si-O		96.9(6)
O-Si-O		116.1(3)
Zr triangular dodecahedron distances (Å) and angles (°)		
Hf-O	[4]	2.115(8)
Hf-O†	[4]	2.260(9)
Average Hf-O		2.188
O-O†	[2]	2.425(16)
O-O	[8]	2.827(13)
O-O††	[4]	3.049(12)
O-O	[4]	2.478(17)
O-Hf-O		64.9(4)
O-Hf-O		80.4(2)
O-Hf-O		68.9(4)
O-Hf-O		92.2(1)
Orientation and magnitudes of hafnium thermal ellipsoids		
Hf	r	0.078(2)A
	r ⊥	0.088(2)A
Cation-cation distances		
Hf-Hf		3.6086(3)
Hf-Si		2.9816(2)
Hf-Si		3.6086(3)

*Bracketed numbers are bond multiplicities.

**Parenthesized figures represent $ed\sigma$'s of the last units cited.

†Edge shared between tetrahedron and dodecahedron.

††Edge shared between two dodecahedra.

Discussion

Comparison with zircon

The unit cell volume of hafnon is 1.24 percent smaller than that of zircon, reflecting the 1.2 percent difference in the Shannon (1976) ionic radius between VIII Hf (0.83 Å) and VIII Zr (0.84 Å). But the ionic radius of Hf is close enough to Zr that the positional parameters of the hafnon structure are identical to previously reported zircon refinements within the errors reported (Robinson *et al.*, 1971; Finger, 1974; Hazen and Finger, 1979). However, the Hf-O distances in hafnon are systematically smaller, a result primarily of the smaller cell dimensions caused by the smaller Hf atom. The average Hf-O distance is 2.188 Å, 0.01 Å smaller than the Zr-O distance of 2.198 Å in zircon (Hazen and Finger, 1979). Of the several zircon refinements at various pressures reported by Hazen and Finger (1979), the hafnon structure corresponds most closely to the 23.2 and 28.9 kbar refinements. They found that the O positional parameters in zircon did not vary between 0 and 50 kbar, and therefore the changes in interatomic distances and angles are related to changes in size of the unit cell. Using their equation

for volume compressibility, synthetic hafnon corresponds to a zircon at 29.5 kbar pressure. This would suggest that hafnon would transform to the scheelite-structure at 30 kbar less than the approximately 120 kbar transition of zircon determined by Reid and Ringwood (1969) and the 160 kbar transition of zircon to the KAlF_4 -structure postulated by Hazen and Finger (1979). Perhaps of more importance, the ubiquitous presence of Hf in solid solution would lower the pressure of any transitions experienced by natural zircons.

Hafnon, zircon and the actinide orthosilicates

The oxygen y and z positional parameters reported for zircon (Hazen and Finger, 1979) are slightly larger than in hafnon, but both are identical within the stated errors. The refinement of a synthetic thorite (Taylor and Ewing, 1978) clearly shows larger values for the oxygen positional parameters (Fig. 1a). This difference of the oxygen position and, more important, the expanded cell dimensions accommodates the larger actinide elements in the zircon-type structure. The z oxygen positional parameter has a larger difference than y with increasing ionic radius for these three isostructural compounds. The resulting positions of the oxygen are at increasing distances perpendicular to the direction joining the two adjacent metal atoms. This allows the greatest increase in bond length with least repositioning of the oxygen. Using the oxygen positional parameters of hafnon, zircon and thorite, values can be predicted for the other actinide orthosilicates (Fig. 1a) as well as the Me-O and Me-O9 bond distances (Fig. 1b) on the basis of their ionic radii.

Hafnon is the only zircon-structure silicate with a metal atom smaller than Zr. Those that remain are natural (Th = thorite, U = coffinite) and synthetic (Pa, Np, Pu, Am) actinide orthosilicates with ionic radii between 0.95 and 1.05 Å. There is complete solid solution between hafnon (Hf = 0.83 Å) and zircon (Zr = 0.84 Å), but some uncertainty regarding the wide miscibility gaps found on the ZrSiO_4 - USiO_4 , ZrSiO_4 - ThSiO_4 , and USiO_4 - ThSiO_4 joins (see Speer, 1980a,b for discussion or references to studies of synthetic and natural orthosilicates). As mentioned above, hafnon is a structural equivalent to a zircon at 29.5 kbar pressure. Using Hazen's (1977) concept that temperature, pressure, and composition are structurally analogous variables, the actinide orthosilicates are structural equivalents of hafnon and zircon at elevated temperatures.

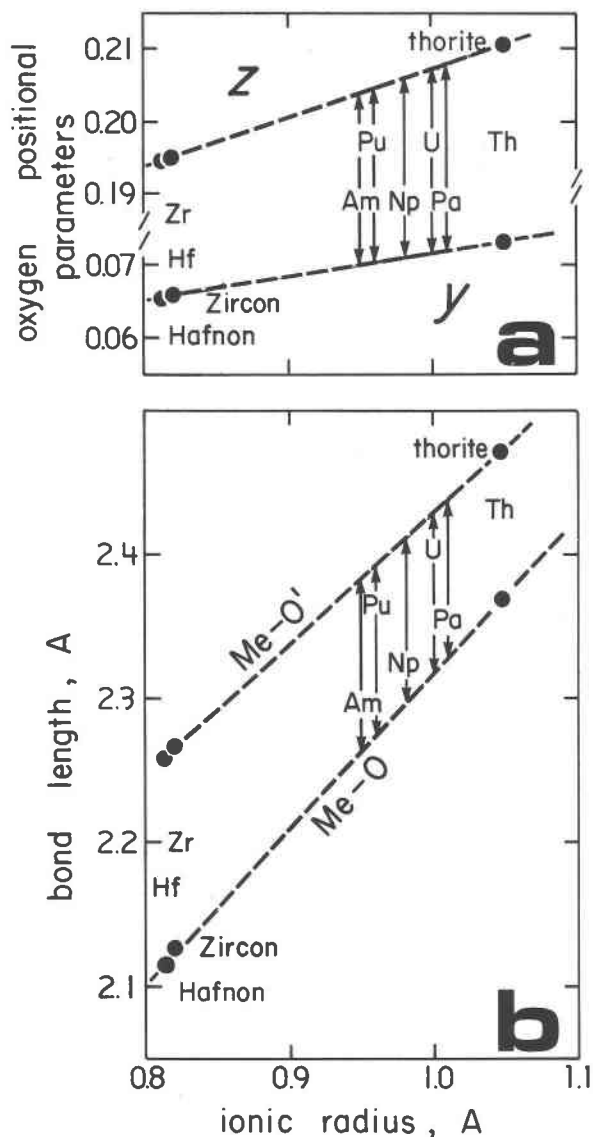


Fig. 1. Variation of the oxygen positional parameters (a) and Me-O and Me-O' bond lengths (b) with ionic radii for the zircon-structure silicates: hafnon (this work), zircon (Hazen and Finger, 1979) and thorite (Taylor and Ewing, 1978). Arrows point to the predicted values for the actinide orthosilicates of Am, Pu, Np, U, and Pa. Ionic radii are from Shannon (1976).

Conversely, hafnon and zircon are structural equivalents of the actinide orthosilicates at high pressures. If the small thermal expansion of zircon (Subbarao and Gokhale, 1968) is characteristic of hafnon, the high-temperature actinide compositional analogues of hafnon and zircon would correspond to values above the melting of zircon and decomposition of hafnon. This would confirm the often observed limited solid solution of actinides in zircon and hafnon. Similarly, if the small compressibility

of zircon (Hazen and Finger, 1979) is characteristic of all zircon-structure silicates, there will be limited solid solution of Zr and Hf in actinide orthosilicates. The differences in ionic radii between the smaller radii zircon-structure silicates (Hf and Zr; 0.83–0.84 Å) and the larger radii ones (Am–Th; 0.95–1.05 Å), makes prediction of limited solid solutions relatively easy. It remains to be seen if the size differences among the actinides are small enough to allow complete solid solutions.

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References

- Cromer, D. T. and Liberman, D. (1970) Relativistic calculations of anomalous scattering factors for X-rays. *Journal of Chemical Physics*, 53, 1891–1898.
- Curtis, C. E., Doney, L. M. and Johnson, J. R. (1954) Some properties of hafnium oxide, hafnium silicate, calcium hafnate, and hafnium carbide. *Journal of the American Ceramic Society*, 37, 458–465.
- Doyle, P. A. and Turner, P. S. (1968) Relativistic Hartree-Fock x-ray and electron scattering factors. *Acta Crystallographica*, A24, 390–397.
- Durif, A. (1961) Structure du germanate d'hafnium. *Acta Crystallographica*, 14, 312.
- Finger, L. W. (1974) Refinement of the crystal structure of zircon. *Carnegie Institution of Washington Year Book*, 73, 544–547.
- Finger, L. W. and Hadjidiacos, C. G. (1981) X-ray diffractometer control system, Krisel Control, Inc. 16 Farsta Court, Rockville, Md. 20850.
- Hazen, R. M. (1977) Temperature, pressure and composition: structurally analogous variables. *Physics and Chemistry of Minerals*, 1, 83–94.
- Hazen, R. M. and Finger, L. W. (1979) Crystal structure and compressibility of zircon at high pressure. *American Mineralogist*, 64, 196–201.
- Ramakrishnan, S. S., Gokhale, K. V. G. K. and Subbarao, E. C. (1969) Solid solubility in the system zircon–hafnon. *Material Research Bulletin*, 4, 323–328.
- Reid, A. F. and Ringwood, A. E. (1969) Newly observed high-pressure transformations in Mn_3O_4 , $CaAl_2O_4$ and $ZrSiO_4$. *Earth and Planetary Science Letters*, 6, 205–208.
- Robinson, K., Gibbs, G. V., and Ribbe, P. H. (1971) The structure of zircon: a comparison with garnet. *American Mineralogist*, 56, 782–790.
- Salt, D. J. and Hornung, G. (1967) Synthesis and X-ray study of hafnium silicate. *Journal of the American Ceramic Society*, 50, 549–550.

- Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751-767.
- Speer, J. A. (1980a) Zircon. In P. H. Ribbe, Ed., *Orthosilicates*, p. 67-112. Mineralogical Society of America *Reviews in Mineralogy* Volume 5.
- Speer, J. A. (1980b) The actinide orthosilicates. In P. H. Ribbe, Ed., *Orthosilicates*, p. 113-135. Mineralogical Society of America *Reviews in Mineralogy* Volume 5.
- Subbarao, E. C. and Gokhale, K. V. G. K. (1968) Thermal expansion of zircon. *Japanese Journal of Applied Physics*, 7, 1126.
- Taylor, M. and Ewing, R. C. (1978) The crystal structures of the ThSiO_4 polymorphs: huttonite and thorite. *Acta Crystallographica*, B34, 1074-1079.

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