Synchrotron X-Ray Rietveld Analysis of α -Hafnium Phosphate

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The crystal structure of α -hafnium bis(monohydrogen orthophosphate)monohydrate, an inorganic ion-exchanger, was solved by the X-ray Rietveld technique utilizing synchrotron radiation (SR) as the X-ray source. This compound is monoclinic with space group $P2_1/n$ and cell parameters $a=9.0142(1)$, $b=5.25665(5)$, $c=15.4768(2)$ Å and $\beta=101.636(1)^\circ$. Intensity data were collected by a capillary method with monochromatic X-rays of wavelength $\lambda=1.49977(1)$ Å. The results were compared with those obtained by a conventional X-ray source and the advantages of SR in Rietveld analysis were verified. Despite the difference in the Li-ion exchange behavior between the α -hafnium phosphate and the α -zirconium phosphate, both phases were found to be isostructural with each other.

Keywords X-ray Rietveld analysis, synchrotron radiation, inorganic ion exchanger, X-ray powder diffraction, α -hafnium bis(monohydrogen orthophosphate)monohydrate

The profile refinement method for analyzing powder-diffraction data, originally devised by Rietveld^{1,2}, has been applied very successfully to neutron powder-diffraction data. On the contrary, fewer papers had appeared concerning the application of this method to X-ray diffraction until recently. However, the X-ray Rietveld method is now being extensively used for the analysis of oxide superconductors³ as well as other ceramic materials and has obtained solid status as an important tool for the structure analysis of powder samples.

On the other hand, synchrotron light sources have also become popular; the application of such light sources to various fields of X-ray analysis is now expanding.⁴ The advantages of synchrotron radiation (SR) over conventional X-ray sources in X-ray powder-diffraction analysis are higher intensity, higher brilliance, a strictly monochromatic beam, wavelength selectivity and a highly collimated parallel beam. Therefore, a combination of the X-ray Rietveld technique and SR as an X-ray source must greatly improve the quality of the diffraction data and, hence, the quality of the analysis. A preliminary study concerning synchrotron X-ray powder diffraction was carried out by Hastings *et al.*, and the advantages of SR in powder-diffraction analysis were demonstrated.⁵ In Japan, a powder diffractometer for SR was constructed in 1981 at the Photon Factory of the National Institute for High Energy Physics and has been used for structural

analyses of amorphous materials and various phase-transition studies using a combination of white X-ray beams and an energy-dispersive method.⁶ However, the diffractometer has not been used to measure diffraction data for the Rietveld analysis of crystal structures using monochromatic X-rays because of the inconvenient setting of the monochromator. Through this experience we have constructed a new power diffractometer, PFPD⁷, which was specially designed for high-resolution powder diffraction at the Photon Factory. The PFPD diffractometer is equipped with a Si(111) monolithic monochromator with a fixed-exit beam position.⁸ This paper reports on the first successful application of the diffractometer to the X-ray Rietveld analysis of a crystalline substance.

To examine the potential ability of the diffractometer in Rietveld analysis we used it to solve the crystal structure of α -hafnium phosphate, $\text{Hf}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -HfP). This material was developed as an inorganic ion-exchanger.⁹⁻¹¹ α -HfP has been believed to be an Hf analog of α -zirconium phosphate (α -ZrP)¹²⁻¹⁴, which is a well-known crystalline inorganic ion-exchanger. However, the Li-ion-exchange behavior of α -HfP is different from that of α -ZrP.⁹ While the crystal structure of α -HfP is not known, that of α -ZrP is. A structure analysis of α -HfP may, therefore, help us to understand the cause of the difference in the ion-exchange behavior between the two materials. Unfortunately, single-crystal structure analysis of α -HfP is

not possible since samples can be synthesized only as a fine powder. The Rietveld technique is therefore practically the only way for determining the crystal structure of α -HfP. A preliminary result of this study was briefly reported elsewhere.¹⁵

Experimental

A powder sample of α -HfP was prepared by the direct precipitation method, as described in the literature¹⁰, and used in subsequent structure analyses. Diffraction measurements were performed at a BL-4B station at the Photon Factory by using the PFPD system. The sample was loaded into a quartz glass capillary of 0.3 mm diameter and mounted on the diffractometer. The capillary was kept rotating by a spinner during data collection.

Intensity data were collected by using the step-scan method under the following conditions: step width = 0.02° in 2θ , measuring time = 10 s/step, D.S. = 0.5 mm, R.S. = 0.3 mm, 2θ range from 10° to 100° . The wavelength of the radiation was adjusted by an Si(111) monolithic monochromator and was determined to be $1.49977(1)\text{\AA}$ by a calibration using an NBS standard reference Si powder. The intensities of the incident X-rays were monitored by measuring the intensities of scattered X-rays from an Al foil situated in the incident beam in front of the sample. The observed intensity data were normalized by the monitor counts. An absorption correction for the cylindrical sample was applied to the intensity data. A Rietveld analysis was made using a FORTRAN program, RIETAN.¹⁶ X-Ray powder diffraction data were successfully indexed with a monoclinic cell with space group $P2_1/n$ (Table 1). Crystal data of α -HfP are compared with those of α -ZrP in Table 1 (Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant digits). Because of the similarities of the crystal data and the powder diffraction patterns between α -HfP and α -ZrP, the structural parameters of α -ZrP¹⁴ were used as the initial values for the structure refinement.

Intensity data were also measured using a conventional X-ray powder diffractometer in order to compare them with SR data. The conditions of data collection were as follows: graphite monochromatized

Cu K_α radiation, step-scan, $0.02^\circ/\text{step}$, 40 s/step, D.S. = S.S. = 0.5° , R.S. = 0.15 mm, flat sample holder of quartz, and 2θ range from 10° to 100° . Intensity data between 10° to 20° measured with the conventional X-ray source could not be used in the structure refinement because of an optical restriction related to the fixed width of the divergence slit.

Results and Discussion

The final atomic parameters obtained by analyses of the SR data are given in Table 2. The final R factors¹⁶ are $R_{wp}=9.16$, $R_p=7.26$, $R_B=10.03$ and $R_F=6.23$ for the SR data (2θ range between 10° and 100°) and $R_{wp}=11.84$, $R_p=9.12$, $R_B=6.28$ and $R_F=2.94$ for the conventional X-ray data (2θ range between 20° and 100°). Figure 1 compares the final Rietveld refinement patterns for the SR data (a) with those for the conventional X-ray data (b). This figure shows the observed profile (dot curve) and calculated one (full curve) with their differences (Δy_i) shown below. As Fig. 1 shows, the diffraction pattern of α -HfP is complex since the lattice parameters of α -HfP are large and the symmetry of the lattice is low, i.e., monoclinic. The peak profile in the SR data (Fig. 1(a)) is much sharper than that in conventional X-ray data (Fig. 1(b)) since the SR beam is highly collimated and lacking the $K_{\alpha 2}$ component. For example, the full width at half maximum (FWHM) of the 200 reflection ($2\theta \approx 20^\circ$) is 0.084° for pattern (a), while it is 0.120° for pattern (b). These observations indicate that the diffraction data measured by the PFPD system are suitable for Rietveld analysis. Diffraction data with a higher resolution could be obtained if we could use a narrower slit system in measurements.⁷

The profile shape function used in RIETAN is an extended pseudo-Voigt function, which can be expressed as a sum of Gaussian and Lorentzian functions.¹⁶ The present analyses indicate that the Gaussian

Table 1 Crystal data for α -HfP and α -ZrP

	α -HfP	α -ZrP ^a
Space group	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	9.0142(1)	9.060(2)
$b/\text{\AA}$	5.25665(6)	5.297(1)
$c/\text{\AA}$	15.4768(2)	15.414(3)
$\beta/^\circ$	101.636(1)	101.71(2)

a. Data taken from ref. 14.

Table 2 Atomic positional parameters and isotropic temperature factors for α -HfP

Atom	x	y	z	$B/\text{\AA}^2$
Hf	0.2459(6)	0.251(6)	0.4855(3)	0.3(1)
P1	0.385(3)	0.74(2)	0.383(1)	0.2(3)
P2	-0.133(2)	0.24(2)	0.396(1)	0.2
O1	0.532(6)	0.80(1)	0.433(3)	1.2(5)
O2	0.340(9)	0.48(1)	0.395(5)	1.2
O3	0.281(9)	0.97(1)	0.406(5)	1.2
O4	0.379(5)	0.75(4)	0.288(3)	1.2
O5	-0.203(9)	0.43(1)	0.437(5)	1.2
O6	-0.177(9)	-0.05(1)	0.424(5)	1.2
O7	-0.194(5)	0.24(4)	0.295(3)	1.2
O8	0.053(6)	0.30(2)	0.406(3)	1.2
O9	0.010(7)	0.73(3)	0.267(3)	1.7(12)

Fig. 1 Rietveld refinement patterns of α -HfP obtained by using (a) SR and (b) a conventional X-ray tube.

fraction was 0.75(4) and 0.37(1) for patterns (a) and (b), respectively. That is, the diffraction profile measured by the PFPD system is fairly close to Gaussian.

Since crystals of α -HfP have plate-like habits, flattened on {001}, the 00/ reflections had a remarkably high intensity because of the preferred orientation effect when the flat sample holder was used in the measurement (see Fig. 1(b)). On the other hand, this effect was negligible in the SR data due to the reduced orientation and rotation of the capillary tube during the measurement (Fig. 1(a)). Further, the effective area of X-ray irradiation does not depend on the diffraction angle in the case of the capillary method. Thus, this method has another advantage that intensity data in a low-angle region ($0 < 2\theta \leq 20^\circ$), which are often very important in the determination of crystal structures, can be used in the analysis. Besides, the capillary tube is advantageous over the flat holder in the analysis of precious samples, because the former requires a much smaller amount of sample than does the latter. The capillary method is also convenient for high- and low-temperature diffraction experiments because of the compactness and airtightness. Therefore, a combination of SR and the capillary method is the best way to collect intensity data for Rietveld analysis.

The crystal structure of α -HfP viewed along the b -axis is illustrated in Fig. 2. α -HfP and α -ZrP are isostructural; namely, α -HfP has a monoclinic unit cell with space group $P2_1/n$ and has a layered structure comprising PO_4 tetrahedra and ZrO_6 octahedra stacked parallel to the (001) plane. Between the layers there are six-sided cavities; water molecules (O9) sit in the centers (Fig. 3). Water molecules are known to be held in the cavities by hydrogen bonds in α -ZrP.¹²⁻¹⁴ There are no interlayer bonds and the layers are held together by only van der Waals forces. The bond distances for α -HfP are given in Table 3 and are compared with those for α -ZrP. The bond distances between the metal atoms and oxygen in the structure of α -HfP are shorter and those between phosphorus and oxygen are longer than the corresponding distances in α -ZrP. Compared with the unit cell of α -ZrP, that of α -HfP expands in the c direction and contracts in the a and b directions. However, the interlayer distance was found to be approximately equal in the two materials.

Here, it is interesting to compare the forms of the two cavities, since exchangeable hydrogen ions are located in the cavities.¹² Figure 3 illustrates the cavities in the structures of (a) α -HfP and (b) α -ZrP. The geometrical forms of the two cavities resemble each

Fig. 2 Crystal structure of α -HfP viewed along the b -axis. Water oxygens (O9) are situated between sheets comprising PO_4 tetrahedra and HfO_6 octahedra.

Table 3 Selected bond distances ($\text{\AA}$) for α -HfP and α -ZrP

α -HfP		
Hf-O1 2.16(1)	P1-O1 1.43(1)	P2-O5 1.41(2)
Hf-O2 2.13(2)	P1-O2 1.49(3)	P2-O6 1.66(3)
Hf-O3 2.00(2)	P1-O3 1.59(3)	P2-O7 1.55(1)
Hf-O5 2.12(2)	P1-O4 1.46(1)	P2-O8 1.69(1)
Hf-O6 1.96(2)	Mean 1.49	Mean 1.58
Hf-O8 1.93(1)		
Mean 2.05		
α -ZrP ^a		
Zr-O1 2.048(2)	P1-O1 1.510(2)	P2-O5 1.517(2)
Zr-O2 2.074(2)	P1-O2 1.512(2)	P2-O6 1.518(2)
Zr-O3 2.071(2)	P1-O3 1.524(2)	P2-O7 1.551(2)
Zr-O5 2.054(2)	P1-O4 1.564(2)	P2-O8 1.519(2)
Zr-O6 2.065(2)	Mean 1.527	Mean 1.526
Zr-O8 2.075(2)		
Mean 2.064		

a. Data taken from ref. 14.

Fig. 3 Cavities in the structure of (a) α -HfP and (b) α -ZrP.

other, except for a minor difference in the oxygen positions. Consequently, it is found that the difference in the Li-exchange behaviors between the two phases is not due to the difference in their crystal structures but,

rather, due to those in some dynamical interactions between the ion exchanger and counter ions: the behavior of the Li-ion exchange is simpler for α -HfP than for α -ZrP; that is, the former exhibits a single-step exchange in contrast to a three-step exchange for the latter.¹¹ This fact shows that the originally isostruc-

tural exchangers behave in a different way in the exchange process, resulting in an intermediate phase in the case of α -ZrP, but no such phase in α -HfP. In other words, two hydroxyl groups in a formula unit have the same apparent acidity in α -HfP, but not in α -ZrP.

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