Structure of 3 at.% and 9 at.% Si-doped HfO₂ from combined refinement of X-ray and neutron diffraction patterns

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Abstract: The crystal structure of 3 at.% and 9 at.% Si-doped HfO₂ powder was determined through refinements using X-ray and neutron diffraction patterns. The lattice parameters, atomic positions, dopant occupancy, and the second phase fraction were determined with high precision using a combined full pattern fitting via the Rietveld method. The results show that both 3 at.% and 9 at.% Si-doped HfO₂ powder exhibit the monoclinic crystal structure with $P 1 2_1/c 1$ space group. Through the combined refinement, the crystal structure parameters, especially for the positions and occupancies of the lighter atoms, were more precisely determined compared to independent X-ray diffraction refinement. Although the ionic radius of Si⁴⁺ is smaller than Hf⁴⁺, with increasing Si occupancy, the unit cell volume slightly increases; possible mechanisms for this effect are discussed. Moreover, the refined results provide evidence of the existence of a non-equilibrium phase of Hf_xSi_{1-x}O₂. The second phase (SiO₂) fraction is determined as 0.17 at.% for 3 at.% Si-doped HfO₂ powders and 1.7 at.% for 9 at.% Si-doped HfO₂ powders.

Keywords: Crystal structure; Rietveld refinement; X-ray diffraction; Neutron diffraction

1 Introduction

Hafnia (HfO_2) is compatible with silicon, SiO_2 , and metal electrodes, and has been used as a high-permittivity thin film gate dielectric for metal oxide semiconductor devices in recent years [1,2]. At certain temperatures and pressures, HfO_2 , which has the fluorite structure, can exhibit displacive transformations [3,4]. Some known polymorphs of HfO_2 include structures in one monoclinic, two orthorhombic, one tetragonal, and one cubic crystal systems. At ambient conditions, HfO_2 exists as a monoclinic phase ($P 1 2_1/c 1$, No.14) without ferroelectric properties because of its centrosymmetric structure [3,4]. However, ferroelectric properties have recently been reported in Si, Al, Y, and Gd-doped HfO_2 thin films, as well as in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films [5-11]. The first ferroelectric investigation was reported by Börscke *et al.* in Si-doped HfO_2 thin films [5]. With Si doping and mechanical encapsulation, it was conjectured that a non-centrosymmetric orthorhombic phase of the $P b c 2_1$ space group was the origin of ferroelectricity in Si-doped 10 nm thick HfO_2 films [5, 12]. In addition, a recent density functional theory calculation based on first-principles identified ferroelectric polarization switching in orthorhombic HfO_2 ($P b c 2_1$ space group) [13]. An improved understanding of the crystal structure of 3 at.% and 9 at.% Si-doped powder HfO_2 may provide insight into the properties of thin film HfO_2 which are employed as a high permittivity dielectric in semiconductor devices and as a ferroelectric thin film in ferroelectric memory devices.

Because crystallographic structural refinement using diffraction data from thin films is unfeasible, we previously determined and reported the structure of Si-doped

HfO₂ from measurements of powder by refining the structure using high resolution X-ray diffraction (XRD) and the Rietveld method [14]. In Ref. [14], the spontaneous ferroelastic strain and the unit cell volume were determined as a function of Si concentration from 3 at% to 10 at%. Unexpectedly, the unit cell volume was shown to increase with Si substitution, even though the ionic radius of Si⁴⁺ is smaller than that of Hf⁴⁺ [15]. While XRD is typically more sensitive to measurement of lattice parameters, neutron powder diffraction is a very useful technique to obtain information about light atoms, e.g. oxygen, in the presence of heavy atoms [16]. Consequently, for Si-doped HfO₂ powder, more precise structural parameters can be obtained by a combined analysis of X-ray and neutron diffraction data because a combined refinement can provide some additional information beyond that obtained from independent analysis of X-ray diffraction data. This has been demonstrated in recent literature, e.g. Refs. [17-19]. In Refs. [17,18], materials structure was redefined according to the combined refinement results in contrast to the independent XRD analysis. In Ref. [19], the ferroelectric properties of (Sr,Ba)Nb₂O₆ were explained from the contribution of Nb atomic position displacement through a combined analysis. Hence, more accurate atomic position data can be obtained from combined refinements, contributing to a more thorough understanding of the structure and properties of Si-doped HfO₂. The present work reports the refined crystal structure of 3 at.% and 9 at.% Si-doped HfO₂ obtained from a combined refinement of high resolution XRD and neutron diffraction.

2 Experimental

Si-doped HfO_2 powders were prepared in a solid-state synthesis process [14]. Reactant powders of HfO_2 (99.95%, Alfa Aesar, Ward Hill, MA) and SiO_2 nanopowders (20-30 nm, 99.5%, Sigma-Aldrich, Milwaukee, WI) were ball milled in ethanol for 24 h. The Si concentration was set at 3 at.% and 9 at.%. Following milling, the slurries were dried, sieved, and calcined at 1400°C for 4 h to obtain Si-doped HfO_2 powders.

Synchrotron-based high resolution XRD patterns of samples were recorded on beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory. The measurement conditions were 295 K, a wavelength of 0.413867 Å, and a 2θ step-size of 0.001° from -6° to 28°. Neutron diffraction patterns were measured on the PULSTAR Research Reactor at North Carolina State University for approximately 7 h using a wavelength of 1.4778142 Å from 10° to 110° at room temperature with a step-size of 0.05°. The same batch of powder was used for both measurements. The diffraction patterns from both instruments were analyzed using a full pattern fitting technique. The crystal structures of the samples were refined using the Rietveld refinement program General Structure Analysis System (GSAS) with the EXPGUI interface [20, 21]. Profile function 4 was used for all the refinements. Si and Hf occupancies were fixed such that they added up to 1, and O occupancies were fixed at 1. Refined parameters included the zero, peak-shape parameters, scale, lattice parameters, atomic positions, isotropic atomic displacement parameters (U_{iso}), atomic occupancies, and the second phase fraction.

3 Results and discussion

3.1 X-ray diffraction refinement

Figs. 1 (a) and (b) show the measured and calculated X-ray diffraction patterns from 3 at.% and 9 at.% Si-doped HfO₂ powders, respectively. Although Si doping has been reported to stabilize the tetragonal phase of ZrO₂ [22], Figure 1 shows that Si-doped HfO₂ remains in the monoclinic phase with up to 9 at.% Si dopant, consistent with the observations in Ref. [14]. More specifically, both 3 at.% and 9 at.% Si-doped HfO₂ powders have a monoclinic crystal structure with space group *P* 1 2₁/*c* 1 (No.14). The quality of fit can be visually seen in the inset figures, specifically in the match between experimental and calculated patterns. For 3 at.% Si-doped HfO₂, the criteria of fit factors are $R_p=6.30\%$ and $\chi^2=3.392$. For 9 at.% Si-doped HfO₂, $R_p=6.23\%$ and $\chi^2=2.424$. These criteria of fit values evidence a satisfactory refinement result. The final values of all refined parameters are shown in Table 1. The lattice parameters and cell volume change with Si doping concentration, implying that a (Hf_xSi_{1-x})O₂ solid solution is formed. As the Si concentration increases from 3 at.% to 9 at.%, the angle β of the unit cell decreased from 99.2357(2)° to 99.2103(3)° with additional changes in lattice parameters *a*, *b* and *c*. From these measurable changes, it can be seen that the unit cell is affected by the Si concentration, or more specifically, by Si occupancy on the Hf site.

In addition, from Fig. 1 and Table 1, it can be seen that there is a small amount of second phase existence in both samples, which is cristobalite SiO₂. The amount of the

second phase slightly increases with increased Si doping concentration. For 3 at.% and 9 at.% Si-doped HfO₂, the refined second phase fractions are 0.17 at.% and 1.69 at.%, respectively. According to the equilibrium phase diagrams, there is no solid solubility of Si in HfO₂ [23,24]. However, the occupancy data identifies the existence of a (Hf_xSi_{1-x})O₂ solid solution, which is considered to be a non-equilibrium phase consistent with earlier results reported in Ref. [14]. The existence of the non-equilibrium nature of (Hf_xSi_{1-x})O₂ is more recently and thoroughly investigated in Ref. [25].

3.2 Neutron diffraction refinement

In contrast to XRD, neutron diffraction is often more sensitive to the positions and occupancies of light elements in the presence of heavy elements. This is because neutron scattering factors do not scale monotonically with atomic number (which is the case for XRD). For oxides such as Si-doped HfO₂, this is useful for determining more accurate O atomic positions and Si occupancy.

The neutron diffraction refinements were completed by fixing the lattice parameters to those from the X-ray diffraction refinement. Background, scale, profile, atomic positions, U_{iso} , atomic occupancies, and zero were refined, using profile function 4. Fig. 2 shows the neutron diffraction pattern refinement results. For 3 at.% Si-doped HfO₂, the criteria of fit factors are $R_p=4.98\%$ and $X^2=1.238$ while for 9 at.% Si-doped HfO₂, $R_p=5.31\%$ and $X^2=1.564$. Similar to the previous independent X-ray diffraction refinement, the crystal structure parameters are also extracted from the refinement results and are listed in Table 1. Compared to the XRD refinement results,

noticeable differences in both the atomic occupancies and positions can be observed in the neutron diffraction refinement results. Moreover, some errors are larger than those in the independent X-ray diffraction refinement results, e.g. the atomic occupancies and Hf positions. In particular, Hf positions have only four decimals accuracy from neutron diffraction, while those from X-ray diffraction have five decimals accuracy. However, it is also noticed that the O positions from the neutron diffraction refinement have little difference relative to those from the X-ray diffraction refinement. Although these results illustrate a lower precision for atomic position and occupancy for the heavier element (Hf) in the neutron diffraction refinement, a higher relative precision is obtained in the neutron diffraction refinement for the lighter O atomic positions. These results show that neutron diffraction is sensitive to the position of lighter elements in the presence of heavy elements. However, the independent neutron diffraction refinement is not sufficient to obtain high-precision atomic structural parameters. This might be due to the weak signal intensity of neutron diffraction in the experiment (Fig. 2).

3.3 Combined refinement of neutron and X-ray diffraction patterns

To take advantage of both X-ray and neutron diffraction measurements, a combined analysis was conducted so that more precise atomic positions and occupancies can be extracted using information from both data sets. In the combined refinement, the lattice parameters, wavelength, and zero offset are fixed. The background, scale, profile, the second phase fraction, atomic positions, U_{iso} , and atomic occupancies are refined to optimize the refinement results. The combined

refinement results are shown in Figs. 3 (a) and (b). In the combined refinement, the X-ray diffraction pattern was fit well ($R_p=6.22\%$ and 6.13% for 3 at.% and 9 at.% Si-doped HfO_2 , respectively); and the neutron diffraction pattern was also fit well ($R_p=5.09\%$ and 5.28% for 3 at.% and 9 at.% Si-doped HfO_2 , respectively). The total R_p for the combined patterns is 6.22% and χ^2 is 3.254 for 3 at.% Si-doped HfO_2 ; for 9 at.% Si-doped HfO_2 , the total R_p is 6.13% and χ^2 is 2.341.

For clear comparison, the crystal parameters obtained by combined analysis are also extracted and shown in Table 1. Compared with the independent X-ray refinement results, the Hf position from combined refinement has little difference, while there are small and visible differences for both O(1) and O(2) positions (Table 1). Moreover, most of the errors from the combined refinement are smaller than in either independent refinement, especially for the Hf and Si occupancies. Smaller errors reflect higher precision, so this result demonstrates that higher precision can be obtained from the combined analysis.

Schematics of the cubic and monoclinic HfO_2 structures are shown in Fig. 4. It appears that the displacements of O are more significant than those of Hf in the monoclinic HfO_2 relative to the cubic HfO_2 . With increasing Si concentration from 3 at.% to 9 at.%, the O(1) position has a clear change in x direction with small changes in the y and z directions (Table 1). The O(2) position has a clear change in the z direction with small changes in the x and y directions. For the Hf position, there are very small changes in x , y and z directions. Correspondingly, the angle β of the monoclinic structure of HfO_2 decreases, reflecting that the unit cell of samples with

different Si concentrations has different unit cell distortions.

The secondary phase (SiO_2) fraction in both samples was calculated in the combined refinement, which is 0.17 at.% and 1.70 at.% for the 3 at.% and 9 at.% Si-doped HfO_2 samples, respectively. The secondary phase fractions obtained from the combined refinement of both samples are very close to those from the independent X-ray refinement analysis (0.17 at.% and 1.69 at.%).

In order to describe the effects of Si doping on unit cell distortion, a scalar spontaneous strain (S) was calculated from the components of the spontaneous strain tensor as described by Salje [26]. The use of the scalar representation of the spontaneous strain allows one single variable to represent the extent of ferroelastic cell distortion that occurs in all directions. The spontaneous strain tensor (e) that describes unit cell distortion from cubic to monoclinic can be written as:

$$e = \begin{pmatrix} e_{11} & 0 & e_{13} \\ 0 & e_{22} & 0 \\ e_{13} & 0 & e_{33} \end{pmatrix} \quad (1)$$

Equations for all non-zero components of the spontaneous strain tensor (e_{ij}) as a function of lattice parameters can be found in the supplemental material [27]. The magnitude of spontaneous strain or scalar spontaneous strain (S) is defined by:

$$S = \sqrt{\sum e_{ij}^2} \quad (2)$$

where $i, j = 1, 2, 3$ and e_{ij} is a component of the spontaneous strain tensor. In this paper, a cubic phase structure was used as the standard symmetric structure to calculate the spontaneous strain S . The spontaneous strain was calculated as 0.11486 for 3 at.% Si-doped HfO_2 sample and 0.11460 for 9 at.% Si-doped HfO_2 sample [14].

With increasing Si occupancy, the unit cell distorts to a structure with lower spontaneous strain.

Table 1 also shows that the unit cell volume measurably increases with increasing Si dopant concentration. As mentioned in the introduction, this is an unexpected result since the ionic radius of Si^{4+} is less than that of Hf^{4+} . Based on arguments of close-packing, the lattice parameter for an ideal cubic fluorite structure can be shown to be approximated as:

$$a = \frac{4}{\sqrt{3}}(r_{\text{cation}} + r_{\text{anion}}) \quad (3)$$

where r_{cation} and r_{anion} are the ionic radii of the cation and anion, respectively. The unit cell volume can then be approximated as a^3 . For Si-doped HfO_2 , r_{cation} of Hf^{4+} with coordination number (CN) of 8 is 0.83 Å [15]. While the ionic radius of Si^{4+} with CN of 8 is not readily available, the value with CN of 4 is 0.26 Å and CN of 6 is 0.40 Å [15]. Using the extrapolation method of Rohrer [28], the ionic radius of Si^{4+} for CN of 8 can be approximated as 0.54 Å. This value is substantially smaller than the ionic radius of Hf^{4+} (by ~35%). According to this simple model (equation (3)) and the ionic radii values, it could be expected that the HfO_2 unit cell volume decreases with increasing Si substitution. Moreover, a calculation of Si-doped *cubic* HfO_2 by Si *et al.* [29] also shows a decrease in cell volume with increasing Si concentration. However, these models are opposite to the trend observed experimentally in the Si-doped HfO_2 monoclinic phase. Some possible mechanisms for this behavior will now be discussed.

While the results in the present work cannot definitively prove the cause of lattice

expansion with Si doping, we can consider several possible mechanisms for such behavior. First, in all oxides, oxygen stoichiometry fluctuations are expected and, in fluorite structures, have been associated with a concept known as chemical expansion [30]. As the concentration of oxygen vacancies increase, it is generally expected that the lattice parameter will decrease due to electrostatic interactions (though there exists converse behaviors proposed in earlier work [31]). Using molecular dynamics and density functional theory, Marrocchelli *et al.* [30] determined that oxygen vacancy formation can drive lattice contraction in CeO_2 and ZrO_2 , fluorite-structured compounds that are similar to HfO_2 . This concept was originally introduced by Glushkova [32] and more recently studied by Omar and Nino [33] and Marrocchelli *et al.* [30]. This behavior can be quantified by describing the effective “volume” of an oxygen vacancy as being less than the volume occupied by ionic oxygen. As an example, Hong and Virkar calculate an oxygen vacancy radius of 0.993 Å compared to an oxygen ionic radius (CN of 4) of 1.38 Å [34]. Based, in part, on the above arguments, it is plausible that the increased unit cell volume with Si substitution could be explained by a decrease in oxygen vacancies (decrease in non-stoichiometry) and associated chemical expansion. Though there is no charge compensation required by substitution of Hf^{4+} by Si^{4+} , it is plausible that the significant difference in ionic size (~35%) may provide a local elastic driving force for a change in oxygen vacancy concentration. This may be related in part by the preference for Si^{4+} to be tetrahedrally coordinated (CN=4), in contrast to the host Hf^{4+} site being cubically coordinated (CN=8).

A second possible mechanism involves one of the cations or anions locating at an interstitial site, which can increase the unit cell volume. Smaller ions (e.g., Si^{4+}) will have a greater tendency for such behavior than larger ions and interstitial alloying is known to occur in CeO_2 and ZrO_2 (e.g., see model introduced by Hong and Virkar [34]). This interstitial mechanism is less likely given that the refined occupancies of Si^{4+} on the Hf^{4+} site are nearly equal to the nominal stoichiometry, though still may be present to some degree.

Because of the significantly smaller ionic radius of Si^{4+} than Hf^{4+} , we also consider that increased electrostatic repulsion may occur between the O^{2-} anions surrounding the Si^{4+} cations. Such an effect may be caused by Si^{4+} displacing from the centrosymmetric position of the Hf^{4+} ion towards a corner or face of the oxygen polyhedron, allowing greater repulsive forces to be realized between the other oxygen ions. This increased repulsion could cause an increase in the unit cell volume.

We also note that the percent of ionicity in the bonds of Si-O and Hf-O is significantly different. From the electronegativity values of the respective elements, it can be shown (e.g., see calculations in Ref. [28]) that the ratio of ionic:covalent character of the Hf-O and Si-O bonds is 0.7:0.3 and 0.51:0.49, respectively. The calculations above that are based on simple arguments of ionic radii are, therefore, overly simplistic. In perovskite solid solutions such as $(\text{Na,Bi,Ba})\text{TiO}_3$ and $(\text{Ba,Ca})\text{TiO}_3$, it has been shown that significant changes in ionicity between different cations and oxygen can result in anomalous lattice parameter changes and phase transition behaviors [35,36]. It is possible that a similar effect occurs in Si-doped

HfO₂. Theoretical modeling might be pursued to test this mechanism.

Finally, we note that the non-equilibrium state of Si-doped HfO₂ is generated through a complex microstructural process involving Si diffusion into the HfO₂ particles [25]. The inhomogeneity of this microstructural process in non-equilibrium state may also affect the oxygen vacancy or interstitial concentrations in ways that could result in unit cell volume expansion. While a definitive mechanism cannot be determined in the present work, the discussion above may provide useful guidance for future experimental or theoretical studies in this area.

4 Conclusions

3 at.% and 9 at.% Si-doped HfO₂ crystal structures were determined by the refinements of X-ray and neutron diffraction via the Rietveld method. The lattice parameters, atomic positions and occupancies, and the second phase molar fraction were obtained with high precision (small errors). Independent X-ray diffraction can determine the second phase fraction and Hf positions, but the O atomic positions are not as accurate. Independent neutron diffraction can provide precise O atom positions, while other structural information, especially atom occupancies, is less accurate. Through combined analysis, the structural parameters of the Si-doped HfO₂ powder, including the Hf and O atomic positions and the Si occupancies on the Hf site were determined with more accuracy relative to the independent X-ray diffraction refinement. Atomic positions with more precision are helpful for visually understand the crystal distortion, and are useful for improving or creating better

structure-property relationships. With increasing Si occupancy on the Hf site, the unit cell distorts towards a structure with lower spontaneous strain and the unit cell volume shows a measurable increase. Some possible mechanisms for this behavior were discussed, including those relating to oxygen vacancy, interstitial concentrations, or ionicity. In the experiment, the non-equilibrium $(\text{Hf}_x\text{Si}_{1-x})\text{O}_2$ coexists with cristobalite SiO_2 . The cristobalite SiO_2 molar fraction is 0.17% and 1.7% for the 3 at.% and 9 at.% Si-doped HfO_2 samples, respectively.

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FIGURE CAPTIONS

Fig. 1. Refinement of XRD pattern of Si-doped HfO₂ powders. The measured XRD pattern is shown in black (×), the calculated fit is in red (-), and the difference pattern is shown below in blue (-). The hkl markers are for HfO₂ (upper), and SiO₂ (lower).

Fig. 2. Refinement of neutron diffraction pattern of Si-doped HfO₂ powders. The measured neutron pattern is shown in black (×), the calculated fit is in red (-), and the difference pattern is shown below in blue (-). The hkl markers are for HfO₂ (upper), and SiO₂ (lower).

Fig. 3. The combined refinement results. The experimental diffraction curves are shown in black (×), the calculated fit is in red (-), and the difference pattern is shown below in blue (-). The hkl markers are for HfO₂ (upper), and SiO₂ (lower). (a) 3 at.% Si-doped HfO₂; (b) 9 at.% Si-doped HfO₂.

Fig. 4. The cubic and monoclinic HfO₂ structure with the spontaneous strain (*S*) of 3 at.% and 9 at.% Si-doped HfO₂ samples

TABLE CAPTION

Table 1. Crystal structure parameters, isotropic displacement parameters, and profile fit values from the combined refinement results

(a) 3 at.% Si-doped HfO₂

(b) 9 at.% Si-doped HfO₂

Fig. 1. Refinement of XRD pattern of Si-doped HfO₂ powders. The measured XRD pattern is shown in black (×), the calculated fit is in red (—), and the difference pattern is shown below in blue (—). The hkl markers are for HfO₂ (upper), and SiO₂ (lower).

(a) 3 at.% Si-doped HfO_2

(b) 9 at.% Si-doped HfO_2

Fig. 2. Refinement of neutron diffraction pattern of Si-doped HfO_2 powders. The measured neutron pattern is shown in black ($\times$), the calculated fit is in red ($-$), and the difference pattern is shown below in blue ($-$). The hkl markers are for HfO_2 (upper), and SiO_2 (lower).

Fig.3 (a) 3 at. % Si-doped HfO_2

Fig.3 (b) 9 at.% Si-doped HfO₂

Fig. 3. The combined refinement results. The experimental diffraction curves are shown in black (×), the calculated fit is in red (—), and the difference pattern is shown below in blue (—). The hkl markers are for HfO₂ (upper), and SiO₂ (lower). (a) 3 at.% Si-doped HfO₂; (b) 9 at.% Si-doped HfO₂.

Fig. 4. The cubic and monoclinic HfO_2 structure with the spontaneous strain (S) of 3 at.% and 9 at.% Si-doped HfO_2 samples

Table 1. Crystal structure parameters, isotropic displacement parameters, and profile fit values from the combined refinement results

Samples		X-ray diffraction		Neutron diffraction		Combined refinement	
		3 at.%	9 at.%	3 at.%	9 at.%	3 at.%	9 at.%
Lattice parameters	a(Å)	5.11714(1)	5.11774(2)	5.11714	5.11774	5.11714	5.11774
	b(Å)	5.17937(1)	5.17608(2)	5.17937	5.17608	5.17937	5.17608
	c(Å)	5.28883(1)	5.29225(2)	5.28883	5.29225	5.28883	5.29225
	β (degrees)	99.2357(2)	99.2103(3)	99.2357	99.2103	99.2357	99.2103
Cell volume (Å ³)		138.356(1)	138.383(1)	138.356	138.383	138.356	138.383
Hf(Si) site	x (Hf,Si)	0.27591(3)	0.27584(4)	0.2770(4)	0.2777(4)	0.27592(3)	0.27585(4)
	y (Hf,Si)	0.04018(3)	0.04010(3)	0.0401(3)	0.0394(4)	0.04018(3)	0.04010(3)
	z (Hf,Si)	0.20745(3)	0.20751(4)	0.2076(3)	0.2080(4)	0.20745(3)	0.20751(3)
	U _{iso} (Å ²)	0.00145(2)	0.00145(2)	0.0028(3)	0.0071(4)	0.00128(2)	0.00145(2)
O(1) site	x(O(1))	0.0743(5)	0.0722(5)	0.0743(5)	0.0726(6)	0.0740(4)	0.0722(4)
	y (O(1))	0.3332(4)	0.3319(5)	0.3359(4)	0.3353(5)	0.3335(4)	0.3334(4)
	z (O(1))	0.3450(4)	0.3457(5)	0.3443(4)	0.3439(4)	0.3450(4)	0.3450(4)
	U _{iso} (Å ²)	0.0040(6)	0.0079(6)	0.0055(5)	0.0128(5)	0.0065(4)	0.0075(4)
O(2) site	x(O(2))	0.4488(5)	0.4495(5)	0.4462(5)	0.4474(5)	0.4487(4)	0.4483(4)
	y (O(2))	0.7585(4)	0.7580(4)	0.7583(5)	0.7576(5)	0.7585(4)	0.7579(3)
	z (O(2))	0.4825(5)	0.4806(5)	0.4800(4)	0.4808(5)	0.4822(4)	0.4805(4)
	U _{iso} (Å ²)	0.0019(6)	0.0072(6)	0.0057(5)	0.0142(6)	0.0050(4)	0.0071(4)
Occupancy	Hf	0.967(4)	0.911(4)	0.984(10)	0.862(10)	0.961(1)	0.913(1)
	Si	0.033(4)	0.089(4)	0.016(10)	0.138(10)	0.039(1)	0.087(1)
SiO ₂ molar fraction		0.17%	1.69%	--	--	0.17%(X-ray)	1.70%(X-ray)
		R _{wp} =8.50%	R _{wp} =8.37%	R _{wp} =6.51%	R _{wp} =7.13%	R _{wp} =8.43%	R _{wp} =8.25%
Profile fit		R _p =6.30%	R _p =6.23%	R _p =4.98%	R _p =5.31%	R _p =6.22%	R _p =6.13%
		χ^2 =3.392	χ^2 =2.424	χ^2 =1.238	χ^2 =1.564	χ^2 =3.254	χ^2 =2.341