Synthesis and X-Ray Structural Analysis by the Rietveld Method of Orthorhombic Hafnia

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斜方晶ハフニアの合成とリートベルト法によるX線構造解析

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Monoclinic hafnia (HfO_2) powders were treated from 400° to 1100°C and at a pressure from 3 to 6 GPa. The products were identified by powder XRD. The results indicated that an orthorhombic phase was synthesized at pressures above 4 GPa in the temperature range from 400° to 1000°C. Although the monoclinic-orthorhombic transition pressure is almost the same as that of ZrO_2 , orthorhombic HfO_2 is more stable at high temperatures than ZrO_2 . The Rietveld analysis showed that the orthorhombic HfO_2 is isostructural with one of the two orthorhombic ZrO_2 (ortho I).

Key-words : Orthorhombic HfO_2 , Phase stability, High pressure polymorphs, High pressure synthesis, Structural analysis, Rietveld method.

1. Introduction

HfO_2 is of interest because of its high melting point and high chemical stability. Its chemical and physical properties are very similar to those of ZrO_2 . HfO_2 , which has monoclinic symmetry at room temperature under atmospheric pressure, transforms to a high pressure phase with orthorhombic symmetry by compression above about 3 GPa.^{1,2)} Present authors performed high pressure synthesis of the orthorhombic HfO_2 in order to determine a formation diagram. The Rietveld analysis of the X-ray diffraction data was also attempted to confirm the structure and to compare it with that of the orthorhombic ZrO_2 . These results will appear in this report.

Fig. 1. Formation diagram of the orthorhombic HfO_2 : (●) recovered sample is the orthorhombic phase; (○) recovered sample is the monoclinic. Dotted lines are the formation diagram of orthorhombic ZrO_2 .⁴⁾

2. High pressure synthesis

The starting material was fine-powders of HfO_2 (grain size was 100 nm) provided by Nacalai Tesque, Inc. The powders had a purity of 98% and contained about 2% of ZrO_2 . The starting material was charged in a platinum capsule and treated at temperatures ranging from 400° to 1100°C and under pressures from 3 to 6 GPa for 30 min by a cubic-anvil-type device.³⁾ The heating temperatures were measured with a Pt/Pt13Rh thermocouple. No correction was made for the pressure dependence of emf, because of its small effect. Phase identification of the recovered samples was made with a microfocused X-ray powder diffractometer.

The orthorhombic HfO_2 was synthesized by quenching at temperatures from 400° to 1000°C and pressures above 4 GPa. Formation diagram of orthorhombic HfO_2 is shown in Fig. 1 together with that of ZrO_2 ⁴⁾ for a comparison. While the monoclinic-orthorhombic transition pressure of HfO_2 is almost the same as that of ZrO_2 , the orthorhombic

Table 1. Final R factors and resulting structural parameters for the two structural models.

Space group : Pbcm Rwp=11.76 Rp=9.48 R _B =8.64					
Atom	Position	g [#]	x	y	z
Hf	4d	1.0	0.2684(6) ^{##}	0.0346(4)	0.2500(7)
O ₁	8e	0.5	0.10(1)	0.39(2)	0.16(2)
O ₂	4c	1.0	0.528(6)	0.25(1)	0.00(2)
a _B =0.50084(1) b _B =0.52274(1) c _B =0.50597(1) nm					
Space group : Pbca Rwp=10.04 Rp=7.75 R _B =6.21					
Atom	Position	g	x	y	z
Hf	8e	1.0	0.8841(2)	0.0344(3)	0.2534(1)
O ₁	8e	1.0	0.796(3)	0.380(6)	0.138(5)
O ₂	8e	1.0	0.977(2)	0.75(1)	0.49(1)
a _B =1.00172(2) b _B =0.52276(1) c _B =0.50598(1) nm					

[#] Site occupancies

^{##} The figures in parentheses indicate the standard deviations as estimated in the refinement.

Fig. 2. Final profile fit and difference patterns for the *PbcA* model. In the upper part, the calculated pattern is drawn and crosses denote the observed intensities. The crosses overlap the calculated pattern and are difficult to distinguish because of the successful profile fit. The lower part shows the differences between the observed and the calculated intensities (DELTA-Y). The markers below the patterns show the possible peak positions from the orthorhombic and the monoclinic.

HfO₂ is more stable at high temperatures compared with ZrO₂.

The samples quenched from temperatures higher than 1000°C in the pressure range above 4 GPa was the monoclinic. It is likely that these samples had been the tetragonal, which is one of the high temperature polymorphs and an unquenchable phase, under high temperature and pressure conditions and converted to the monoclinic on releasing pressure.

3. Rietveld analysis

X-ray diffraction data were collected using Cu K α radiation and a θ - 2θ diffractometer with a curved-graphite monochromator positioned on the diffracted beam side. The counting time was 8s at each step of 0.02° over the 2θ range from 20° to 110°.

The Rietveld analysis was performed by the use of a program RIETAN.⁵⁾ No correction on preferred orientation was made because the high pressure sample consisted of a fine grain (100 nm). As a small amount of the monoclinic phase coexisted in the sample, the recorded pattern was analyzed assuming a two-phase mixture of the monoclinic and the orthorhombic. In the two-phase refinement, a matrix refinement of the orthorhombic structure with the variables of the scale factor, lattice parameters, fractional coordinates and individual isotropic thermal parameters was undertaken along with the refinements of the scale factor and lattice parameters of the monoclinic structure, while fractional coordinates and individual isotropic thermal parameters of this phase were fixed for the reported values.⁶⁾

On the basis of TEM observations, Raman spectra analyses and comparisons with the monoclinic structure, several structural models were proposed for the orthorhombic HfO₂ and ZrO₂.^{2,7)-10)} Among these models, *R* factors were reasonably reduced when following two models were used: One is a model with *Pbcm* symmetry,²⁾ which is reported for

the orthorhombic HfO₂. The other is a model with *Pbca* symmetry,⁷⁾ which is our recent results for an orthorhombic ZrO₂. The final *R* factors, the resulting structural parameters and their standard deviations for each model are listed in Table 1. These results support the structure of *Pbca*. The final profile fit and difference patterns are plotted against 2θ in Fig. 2. It is concluded that the orthorhombic HfO₂ is isostructural with an orthorhombic ZrO₂.

As shown in Table 1, however, the standard deviations for the structural parameters of oxygen are considerably large. This result indicates that the configuration of oxygen framework is difficult to be fixed by the present X-ray powder diffraction method. As the X-ray scattering factor of oxygen is considerably small compared with that of hafnium, the authors are planning neutron diffraction experiments of this phase in order to determine the accurate configuration of oxygen framework.

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