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Phase Relations and Volume Changes of Hafnia under High-Pressure and High-Temperature

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Introduction

Under high-pressure conditions, HfO_2 has two high-pressure polymorphs both of which have orthorhombic symmetries and are denoted as orthoI and orthoII, respectively. In the present study, we have performed a series of high-pressure and high-temperature in situ observations using multi-anvil high-pressure devices and synchrotron radiation in order to elucidate the phase relations among high-pressure polymorphs and their elastic properties.

Experimental

Polycrystalline HfO_2 powder with nominal purity of 98% (2% of ZrO_2 is contained) was pelletized and encased in a sample chamber. A mixture of synthetic orthoI and Au powders (5:1 by weight ratio) was also put in the sample chamber separately. Generated pressure was estimated using the lattice constants of Au based on the equation of state. Because Hf ions absorb X-ray strongly, thickness of the sample was about 800 μm . X-ray observations under high pressure and temperature were carried out using MAX80 system with sintered diamond anvils of 3 mm truncation at AR-NE5C station of National Laboratory for High Energy Physics. The incident x-ray beam was collimated to 0.1 mm in height and 0.3 mm in width, and diffracted x-ray was measured with a pure germanium solid-state detector (SSD) by an energy dispersive method. The energy range used for the analysis was approximately 40-80 keV.

Results and discussion

Obtained phase diagram of HfO_2 under high-pressure and high-temperature is shown in Fig. 1, where the observed four phases are labeled by different symbols. The monoclinic-orthoI phase boundary locates at 4 GPa and is almost independent of temperature. This result is in good agreement with a previous boundary determined by synthesis experiments. The extrapolation of the boundary to room temperature is about 4 GPa. The orthoI-tetragonal boundary lies between 1250 and 1400 °C and has a slight positive dT/dP slope. This almost pressure independent phase boundary indicates that pressure has little effect on this transition. Calculated volumes of orthoI (1350 °C) and tetragonal (1400 °C) at 10.5 GPa are 130.2 and 131.5 A^3 (z=4), respectively and are practically the same. Determined orthoI-orthoII boundary lies at 14.5 GPa and is almost temperature independent. By compression at room temperature, orthoII is reported to appear above about 30 GPa. This fact indicates that the orthoI-orthoII transition becomes increasingly sluggish under low temperature because the transition is a reconstructive-type. Once formed orthoII phase is quenchable to ambient conditions.

The unit cell parameters and the volumes of orthoI and orthoII have been determined as the functions of pressure and temperature. The orthoI-orthoII transition accompanies about 8 % volume decrease. The bulk moduli calculated using Birch-Mughnahan's equation of state are 220 and 312 GPa for orthoI and orthoII, respectively. The present result indicates that orthoII is highly incompressible and thus a candidate for ultra hard materials.

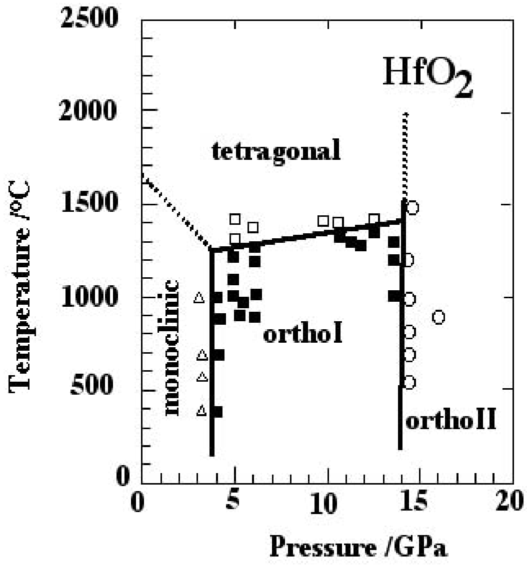

Figure 1 Pressure-temperature phase diagram of HfO_2 determined from the in-situ X-ray diffraction measurements. Open triangles, close squares, open squares and open circles represent the monoclinic, orthoI, tetragonal and orthoII, respectively. Dotted lines are assumed boundaries.

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