Phase Relations and Equations of State of ZrO2 under High-Temperature and High-Pressure
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Phase Relations and Volume Changes of Hafnia under High-Pressure and High-Temperature
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1. Phase relations and equations of state of ZrO_2 under high-temperature and high-pressure

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The phase relations and pressure volume dependences of ZrO_2 under high-pressure and high-temperature have been investigated by means of *in situ* observation using multi-anvil type high- pressure devices and synchrotron radiation. By compression of 3-4 GPa, baddeleyite (monoclinic ZrO_2) transforms to two distorted fluorite (CaF_2)-type phases depending on temperature: an orthorhombic phase, orthoI, below 600 °C and a tetragonal phase above 600 °C. Both orthoI and tetragonal phases then transform into another orthorhombic phase, orthoII, with a cotunnite ($PbCl_2$)-type structure above 12.5 GPa and the phase boundary is almost independent of temperature. OrthoII is stable up to 1800 °C and 24 GPa. The unit cell parameters and the volumes of these high-pressure phases have been determined as functions of pressure and temperature. The orthoI/tetragonal-to-orthoII transition accompanies about 9 % volume decrease. The thermal expansion coefficient of orthoII at 20 GPa is $2.052\pm0.003\times10^{-5}K^{-1}$ over 25-1400 °C. The bulk modulus calculated using Birch-Murnaghan's equations of state is 296 GPa for orthoII, which suggests that the high density ZrO_2 is a candidate for potentially very hard materials. The phase relation of stabilized cubic ZrO_2, $CaO\text{-}ZrO_2$, under pressure at elevated temperature has also been examined. Distorted fluorite-type phases do not appear in $CaO\text{-}ZrO_2$ but the direct transition from cubic phase to orthoII is observed on the same P-T conditions as in pure ZrO_2.

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

Ohtaka et al.,

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Utilizing multi-anvil high-pressure devices and synchrotron radiation, X-ray in situ observations of hafnia under high-pressure and high-temperature have been performed to investigate its phase relations and compression behavior. An orthorhombic phase (orthoI) is stable from 4 to 14.5 GPa below 1250-1400 °C and transforms to a tetragonal phase, which is one of the high-temperature forms of HfO_2, above these temperatures. Another orthorhombic phase (orthoII) with a cotunnite-type structure appears above 14.5 GPa. OrthoII is stable up to 1800 °C at 21 GPa. OrthoII is quenchable to ambient conditions. The orthoI-orthoII transition is accompanied by about 8 % volume decrease. The bulk moduli of orthoI and orthoII at room temperature are 220 and 312 GPa, respectively. This low compressibility of orthoII indicates that it is a potential candidate for very hard materials.