

Post-Cotunnite Phase Transition in Zirconia at High Pressure

A post-cotunnite phase transition in zirconia was investigated up to 200 GPa and 3000 K by a diamond anvil cell and synchrotron X-ray diffraction measurements. The experiments demonstrated that the cotunnite phase was stable up to 170 GPa and 2000 K, and the Fe₂P-type phase appeared in association with the cotunnite phase above 3000 K. This is the first experimental evidence of the cotunnite to Fe₂P-type phase transition in zirconia. The close structural relationship of two phases can be well explained using the oxygen-zircon polyhedra, and the cotunnite to Fe₂P-type phase transition is a common trend in many dioxides under high pressure.

Zirconia (ZrO₂) is well known as an important class of material because of its attractive ceramic properties. The high-pressure behavior of zirconia has also been the focus of considerable study in order to understand the densification mechanism in dioxides as an analogue of important terrestrial dioxides such as silica. Zirconia transforms to the cotunnite phase at 13 GPa and the post-cotunnite phase transition has been examined in the past decade. However, no transition has been found at least up to 100 GPa [1]. Recently, *ab initio* calculations have predicted that the cotunnite phase transforms to the Fe₂P-type phase in titania, and this transition was experimentally demonstrated at 200 GPa and 4000 K [2]. Zirconium belongs to the same group as titanium in the periodic table, while it has a larger ionic radius. This suggests that zirconia should behave as a low-pressure analogue of titania. This work investigated the post-cotunnite phase transition in zirconia up to 200 GPa and 3000 K [3].

Experiments were performed by a laser heated diamond anvil cell combined with synchrotron radiation X-ray diffraction measurements. Beveled anvils with 100–300 μm culets were mainly used. Zirconia powder with a small amount of platinum, which acts as a pressure marker, was placed in the gasket hole with NaCl pellets. Heating was conducted using focused fiber lasers from both sides of the sample. Angle-dispersive X-ray diffraction measurements using monochromatic X-ray radiation at 30 keV were taken in situ at high pressure and room temperature after heating.

In the first run, the cotunnite phase was still observed at 148 GPa and room temperature after heating (Fig. 1a). In the second run, the cotunnite phase was also observed at 170 GPa and room temperature after heating at 2000 K, while new X-ray diffraction lines appeared by heating above 3000 K. All the peaks of the X-ray diffraction pattern at 171 GPa after heating can be indexed by the mixture of the cotunnite and Fe₂P-type phases (Fig. 1a). This is the first experimental evidence of the cotunnite to Fe₂P-type phase transition in zirconia. The X-ray diffraction patterns of this sample were also obtained during decompression with heating, and the coexistence was observed down to 76 GPa after heating. Under 50 GPa, the Fe₂P-type phase disap-

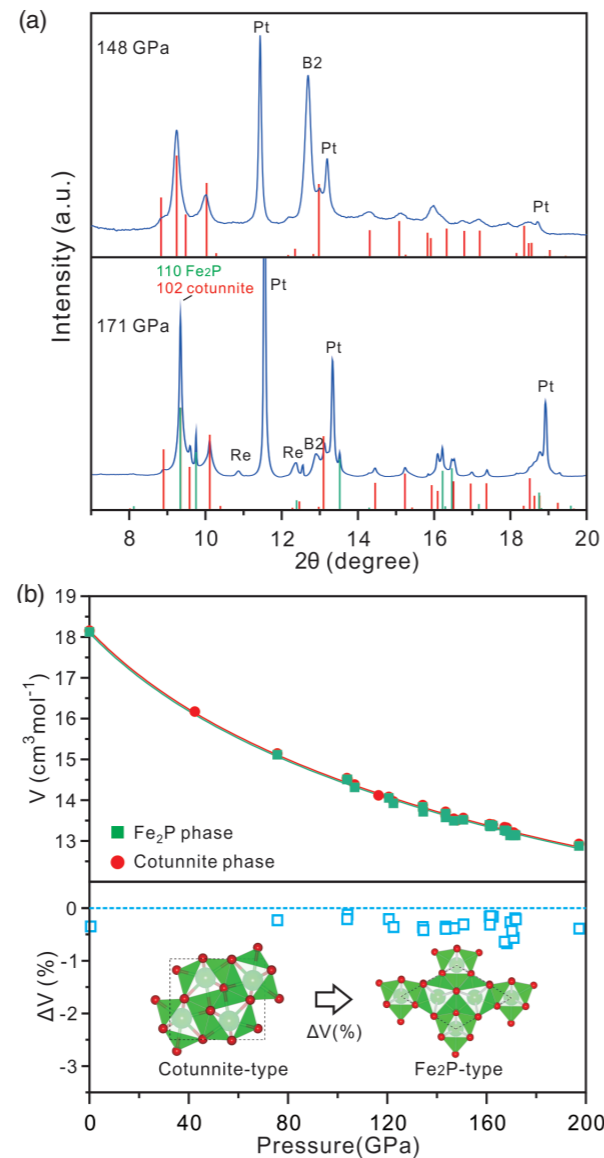


Figure 1: (a) Representative X-ray diffraction patterns of the cotunnite phase (red line) and the Fe₂P-type phase (green line) at high pressure and room temperature after heating. (b) Volume change of the cotunnite phase (red circles) and the Fe₂P-type phase (green squares) and its difference (open blue squares).

Cotunnite structure

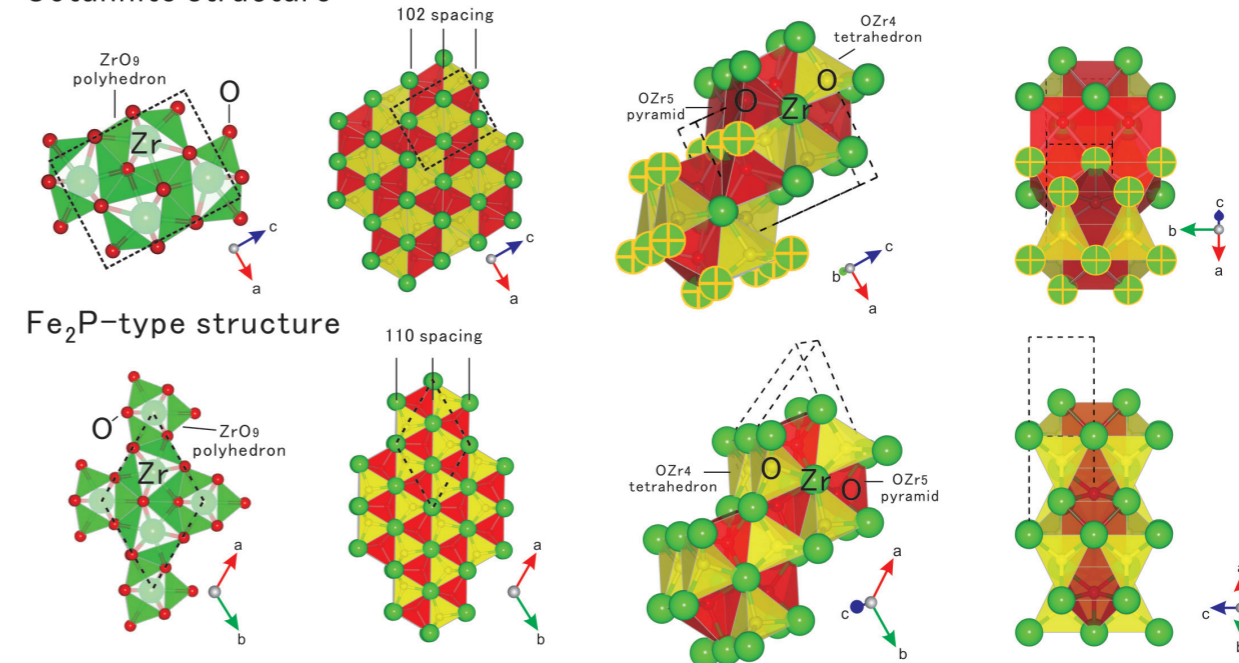


Figure 2: The structures of the cotunnite and Fe₂P-type phases. The structures are drawn using oxygen-zircon polyhedra to assist visual understanding of the differences. The models using standard zirconium-oxygen polyhedra are also shown on the left side for comparison. The Fe₂P-type structure model can be derived by the 1/2 period shift of several zirconium lines (marked by crosses) parallel to the cotunnite *b*-axis.

peared and only the cotunnite phase remained. In the third run, the sample was compressed to 200 GPa and then heated at 3000 K. The Fe₂P-type phase appeared, while the cotunnite phase still remained. This sample was recovered to the ambient condition without heating, and both phases were maintained. This is the first example of an Fe₂P-type oxide quenched to ambient conditions.

The unit cell volume of the Fe₂P-type phase was consistently smaller than that of the cotunnite phase (Fig. 1b), indicating that the Fe₂P-type phase is the higher pressure phase. Indeed, the Fe₂P-type phase disappeared earlier than the cotunnite phase during decompression with heating. However, the volume difference was quite small (~0.6% Δ*V*) and both phases coexisted over a wide pressure range (Fig. 1b). These are attributable to slow kinetics by a structural similarity. Although the crystal structures of both phases consist of a network among the ZrO₉ polyhedra (Fig. 2), it is difficult to show the structural difference on this basis. Therefore, we propose that the structures should instead be drawn using oxygen-zircon polyhedra rather than zirconium-oxygen polyhedra. Using this description, the structural unit can be described as OZr₄ tetrahedra and OZr₅ pyramids (Fig. 2). The arrangement of polyhedra is different between the structures, while the Fe₂P-type structure can be derived from the cotun-

nite structure by simple operation: the 1/2 shift of the zirconium lines in the cotunnite structure parallel to the *b*-axis of the cotunnite-type cell (Fig. 2). The structural similarity may result in slow kinetics for the phase transition, explaining why coexistence was observed over a wide pressure range. The cotunnite to Fe₂P-type phase transition was experimentally demonstrated in zirconia [3] (this study) and titania [2], and predicted in germania [4] and silica [5], suggesting that it is a common trend in many dioxides under high pressure.

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