

The pressure-induced structural response of $A_2Hf_2O_7$ (A=Y, Sm, Eu, Gd, Dy, Yb) compounds from 0.1-50 GPa

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$A_2B_2O_7$ (A, B= cations) compounds have elegant structures that make their properties conducive to a variety of applications; one example is that they are a proposed waste-form for actinides generated in the nuclear fuel cycle. Part of the reason for the interest in these applications is because of their structural response in extreme environments of high P, high T, and under intense irradiation. Depending on their cationic radius ratio, r_a/r_b , $A_2B_2O_7$ compounds either crystallize as pyrochlore ($r_a/r_b=1.3-1.7$) or “defect fluorite” ($r_a/r_b>1.3$). Pyrochlore and “defect-fluorite” structure types are similar: they are derivatives of an ideal fluorite structure with two cations and 1/8 missing oxygen anions. In pyrochlore-structured oxides, the cations, A and B, as well as the anion vacancy, are ordered. In “defect fluorite”-structured oxides, the cations and anion vacancies are disordered. $A_2B_2O_7$ compounds rarely amorphize in extreme environments. Rather, they often disorder and undergo phase transitions; this resistance to amorphization contributes to the durability of this potential actinide waste-form. Under high-pressure conditions, $A_2B_2O_7$ compounds are known to disorder, and sometimes form a cottunite-like phase. Their radius ratio affects their response to extreme environments; “defect fluorite” type compounds tend to disorder, and pyrochlore type compounds tend to form the cottunite-like phase. In this study, we have examined six $A_2Hf_2O_7$ compounds (A=Y, Sm, Eu, Gd, Dy, Yb) *in situ* to pressures up to 50 GPa. By keeping the B-site constant (Hf), we examined the effect of a changing radius ratio on the pressure-induced structural response of hafnates. We used symmetric DACs (300 μm culets), ruby fluorescence, stainless steel gaskets, and methanol: ethanol (4:1 by volume) pressure medium. We characterized these materials with *in situ* Raman spectroscopy at Stanford University, and synchrotron X-Ray Diffraction (XRD) at APS 16 BM-D and ALS 12.2.2. The compounds studied in this experiment corresponded to two groups, the pyrochlore structured (Sm, Eu, Gd) hafnates, and the “defect-fluorite” structured hafnates (Y, Dy, Yb). These compounds undergo a slow phase transition to a high-pressure cottunite-like phase between 18-30 GPa. They undergo disordering of their cation and anionic sites as pressure is increased. The pressure of their phase transitions depends on their radius ratio. Our results are comparable to many high-pressure studies of rare earth zirconates and titanates, but contrast from previous experiments performed on rare earth hafnates, specifically $La_2Hf_2O_7$.