The pressure-induced structural response of rare earth hafnate and stannate pyrochlore from 0.1-50 GPa

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Complex oxides with the pyrochlore ($A_2B_2O_7$) and defect-fluorite ($(A,B)_4O_7$) structure-types undergo structural transformations under high-pressure. These compounds are a proposed waste-form for actinides generated in the nuclear fuel cycle. High-pressure transformations in rare earth hafnates ($A_2Hf_2O_7$, A=Sm, Eu, Gd, Dy, Y, Yb) and stannates ($A_2Sn_2O_7$, A=Nd, Gd, Er) were investigated up to 50 GPa and characterized by *in situ* Raman spectroscopy and synchrotron x-ray diffraction (XRD). At ambient pressure all compositions, including the defect-fluorite structured hafnates (A=Dy, Y, Yb), have pyrochlore-type short-range order. Hafnates and stannates underwent a pressure-induced phase transition to a cotunnite-like structure that begins between 18-25 GPa in hafnates and between 30-33 GPa in stannates. The transition was not complete at 50 GPa; upon decompression, XRD indicates that all compositions transform to defect-fluorite with an amorphous component. Disordering in stannates and hafnates occurs gradually upon compression. Hafnates and stannates decompressed from 50 GPa show Raman spectra consistent with weberite-type structures, also reported in irradiated stannates. The second-order Birch-Murnaghan equation of state fit gives a bulk modulus of ~250 GPa for hafnate compositions with the pyrochlore structure, and ~400 GPa for hafnate compositions with the defect-fluorite structure. Stannates have a lower bulk modulus relative to hafnates. Stannate and hafnate pyrochlore compositions taken to high pressure show structural transformations consistent with irradiated pyrochlore and compositionally disordered pyrochlore: a long-range structure best described by defect-fluorite, and a short-range structure best described by weberite.