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 under consideration for applications including as 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). Rare-earth hafnates ($A_2Hf_2O_7$) form the pyrochlore structure for A=La-Tb and the defect-fluorite structure for A=Dy-Lu. Lanthanide stannates form the pyrochlore structure. Raman spectra revealed that at ambient pressure all compositions, including the defect-fluorite hafnates, have pyrochlore-type short-range order. Stannate compositions show a larger degree of pyrochlore-type short-range ordering relative to hafnates. *In situ* high-pressure synchrotron XRD showed that rare earth hafnates and stannates underwent a pressure-induced phase transition to a cotunnite-like (*Pnma*) structure that begins between 18-25 GPa in hafnates and between 30-33 GPa in stannates. The phase transition is not complete at 50 GPa, and upon decompression, XRD indicates that all compositions transform to defect-fluorite with an amorphous component. I*n situ* Raman spectroscopy showed that disordering in stannates and hafnates occurs gradually upon compression. Pyrochlore-structured hafnates retain short-range order to a higher pressure (30 GPa vs. <10 GPa) than defect-fluorite-structured hafnates. 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. $Dy_2Hf_2O_7$ is intermediate in its response, with some pyrochlore-type ordering, based on Raman spectroscopy and the equation of state, with a bulk modulus of ~300 GPa. Stannates have a lower bulk modulus relative to hafnates (between 80-150 GPa). 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.