Lanthanide stannate pyrochlores (Ln$_2$Sn$_2$O$_7$; Ln= Nd, Gd, Er) at high pressure

Katlyn M. Turner$^*$, Cameron L. Tracy$^1$, Wendy L. Mao$^1$, & Rodney C. Ewing$^1$

$^1$: Department of Geological Sciences, Stanford University

*Corresponding author: katlynmt@stanford.edu

Pyrochlore-structured oxides (A$_2$B$_2$O$_7$; Fd-3m) undergo phase transitions in extreme environments. In order to examine pressure-induced transformations in pyrochlore oxides (A$_2$B$_2$O$_7$; Fd-3m), lanthanide stannate pyrochlores (Ln$_2$Sn$_2$O$_7$; Ln=Nd, Gd, Er) were studied in situ under compression up to ~50 GPa. Stannates were investigated because the <Sn-O> bond is more covalent that that in Ti, Zr, and Hf pyrochlores that have been previously studied in extreme environments. This also provides an opportunity to examine the role of the cation radius ratio, r$_{Ln}$/r$_{Sn}$, on phase transitions in a covalently bonded pyrochlore. Raman spectroscopy indicated that stannates begin to disorder at 0.3 GPa; the extent of disorder vs. pressure is greater in stannates with a smaller cation radius ratio. X-ray diffraction revealed that stannates begin a slow transformation to a cotunnite-like (Pnma) structure at ~28 GPa. This transition has been observed in other pyrochlore compositions, but unique to stannates, the onset pressure is constant rather than varying with the cation radius ratio, which ranges between 1.46-1.61 in the stannates studied. Additionally, the extent of the transition vs. pressure varies among compositions, with no correlation to the cation radius ratio. Similar to pyrochlore zirconates and hafnates, the bulk moduli of stannates are inversely correlated with the cation radius ratio. Post decompression from ~50 GPa, Gd$_2$Sn$_2$O$_7$ and Er$_2$Sn$_2$O$_7$ adopt a pyrochlore structure, which is unique from all other pyrochlores studied under compression. Nd$_2$Sn$_2$O$_7$ adopts a multi-scale structure that is long-range defect-fluorite and short-range weberite when quenched from high-pressure, which is more typical of pyrochlore zirconates, hafnates, and titanates. Overall, the behavior of stannate pyrochlore at high pressure suggests that combined influences of <Sn-O> bond covalence and the cation radius ratio of Ln$^{3+}$/Sn$^{4+}$ control the structural response to compression.