Unraveling Structural Details in Negative Thermal Expansion Materials
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Negative thermal expansion (NTE) materials have attracted significant attention over the past two decades. The phenomenon of contraction during heating has been known for a long time through the “density anomaly of water” discovered in the 1800’s, and Scheel’s expansion measurements on quartz and vitreous silica in the early 1900’s. However, it was not until the 1990’s that detailed crystallographic studies brought tremendous growth to this field. For several families of NTE materials (ZrV$_2$O$_7$-, ZrW$_2$O$_8$- and Sc$_2$W$_3$O$_{12}$-families), knowledge of the crystal structure combined with variable temperature diffraction studies could demonstrate that the negative volume expansion was a direct result of low energy phonon modes that led to concerted tilting motions of the corner-sharing polyhedral networks.

While much progress has been made in elucidating the structural basis of the NTE phenomenon, phase transitions as a function of composition, temperature and pressure are much less understood. This talk will focus on the scandium tungstate (A$_2$M$_3$O$_{12}$) family, which can adopt a very wide range of compositions. In this family, NTE is observed in an orthorhombic structure (space group Pnca), but many compositions show a reversible phase transition to a structurally related denser monoclinic polymorph (space group P2$_1$/a) with positive expansion upon cooling. This structure is also commonly observed at very low pressures (<0.6 GPa) upon compression. The M-site generally contains Mo or W, while the A-site can be substituted by trivalent cations ranging in size from Al$^{3+}$ to the smaller lanthanides, or by mixtures of di- and tetravalent cations. Materials containing mixtures of Mg$^{2+}$ and Zr$^{4+}$ or Hf$^{4+}$ have also been reported. These compositions crystallize in a cation ordered variant (space group Pna2$_1$) of the orthorhombic Pnca structure, which was investigated by high resolution synchrotron diffraction. The high pressure behavior of these MgA’M$_3$O$_{12}$ materials was also studied using synchrotron diffraction. Subtle phase transitions were observed through anisotropic peak shifts, but the data could be described with the ambient pressure orthorhombic cell up to the pressures where amorphization was observed.