



Cora Lind-Kovacs, PhD
University of Toledo

Negative Thermal Expansion Materials Structural Studies and Tuning of Properties

ABSTRACT: 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 (ZrV₂O₇-, ZrW₂O₈- and Sc₂W₃O₁₂-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 (A₂M₃O₁₂) family, which can adopt a very wide range of compositions. The M-site generally contains Mo or W, while the A-site can be substituted by trivalent cations ranging in size from Al³⁺ to the smaller lanthanides, or by mixtures of di- and tetravalent cations. 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 P2₁/a) with positive expansion upon cooling. This structure is also commonly observed at very low pressures (<0.6 GPa) upon compression. Materials containing mixtures of Mg²⁺ and Zr⁴⁺ or Hf⁴⁺ crystallize in a cation ordered variant (space group Pna2₁) of the orthorhombic Pnca structure, which shows kinetically sluggish behavior during heating and cooling cycles. The high pressure behavior of these MgA’M₃O₁₂ 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.

BIO: Cora Lind-Kovacs is a Professor in the Department of Chemistry and Biochemistry at the University of Toledo. As an undergraduate, she studied chemistry at the University of Wuppertal, Germany, and obtained her prediploma in chemistry in 1996. She received her Master’s and Ph.D. degrees in chemistry under Angus Wilkinson from the Georgia Institute of Technology in 1999 and 2001, respectively, and conducted postdoctoral research with Frank DiSalvo at Cornell University. In 2003, she started her independent career as an Assistant Professor at the University of Toledo, where she was subsequently promoted to Associate (2008) and Full (2014) Professor. Her research interests are focused on the synthesis and characterization of negative thermal expansion materials and the preparation of inorganic/polymer composites. Her group heavily relies on diffraction methods, including powder X-ray and neutron diffraction under non-ambient temperatures and pressures. Cora currently serves as Chair of the U.S. National Committee for Crystallography, and has received several awards, including the ACA’s Etter Early Career Award and the ACS PROGRESS/Dreyfus Lecturer award.