

Poster Presentation

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Phase behavior and thermoelastic properties of SnMo₂O₈ under hydrostatic pressure

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SnMo₂O₈ has been shown to exhibit very different phase behavior and thermal expansion from previously studied members of the AM₂O₈ family.¹ At high temperatures, SnMo₂O₈, ZrW₂O₈, and ZrMo₂O₈ assume cubic structures with orientationally disordered MO₄ tetrahedra; however, their behavior is widely divergent at lower temperatures. ZrMo₂O₈ maintains its disordered structure and continues to display negative thermal expansion (NTE). While cubic symmetry is retained when cooling ZrW₂O₈, its WO₄ tetrahedra become ordered, and its NTE increases in magnitude. Rapid cooling of SnMo₂O₈ leads to a cubic structure that only minimally differs from its high temperature form.¹ Slowly heating this cubic phase results in a transformation to a rhombohedral (γ) structure with ordered MoO₄ tetrahedra that is not isostructural to any known phases of ZrW₂O₈ and ZrMo₂O₈.¹ In stark contrast to ZrW₂O₈, and ZrMo₂O₈, all SnMo₂O₈ phases exhibit positive thermal expansion.¹ In the current work, the phase behavior and thermoelastic properties of cubic SnMo₂O₈ under hydrostatic conditions were investigated via in situ synchrotron x-ray powder diffraction in a recently designed sample environment.² Previous studies of ZrW₂O₈ and ZrMo₂O₈ in this environment have shown that pressure-induced disordering of MO₄ tetrahedra, which only occurred in the orientationally ordered low temperature ZrW₂O₈ phase, was linked to both elastic softening on heating and enhancement of NTE.³ At 298K, cubic SnMo₂O₈ is significantly softer ($\kappa T = 30\text{GPa}$) than ZrW₂O₈ (64GPa) and ZrMo₂O₈ (43GPa).³ Unlike ZrW₂O₈, which softens upon heating to 516K ($\Delta\kappa T = -9\text{GPa}$), SnMo₂O₈ stiffens (+5GPa) more than ZrMo₂O₈ (+2GPa).³ The phase behavior of SnMo₂O₈ under pressure also differs from that of ZrW₂O₈ and ZrMo₂O₈. Compression elevated the $\gamma \rightarrow$ cubic transition temperature significantly: at ambient temperature, this transition occurs at $\sim 435\text{K}$; at 310MPa, it occurs at $\sim 490\text{K}$.

[1] S. E. Tallentire, F. Child, I. Fall et al, *J. Am. Chem. Soc.*, 2013, 135, 12849, [2] A. P. Wilkinson, C. R. Morelock, B. K. Greve et al, *J. Appl. Crystallogr.*, 2011, 44, 1047, [3] L. C. Gallington, K. W. Chapman, C. R. Morelock et al, *Phys. Chem. Chem. Phys.*, 2013,15, 19665

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