

Poster Presentations

[MS20-P13] Pressure-Dependent Behaviour and Origin of Negative Thermal Expansion in Zinc Cyanide.

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Zinc (II) cyanide, $\text{Zn}(\text{CN})_2$, a canonical cyanide framework of antiperovskite topology, has attracted considerable attention over the last ten years due to its very large isotropic negative thermal expansion (NTE) response. Over its entire stability range, the cubic lattice parameter, a (and hence volume, V) decrease monotonically as temperature increases, taking the expansivity $\alpha_V = -50.7(6) \text{ MK}^{-1}$ over the range 25–375 K [1]. This unusual thermal response is matched by very complex, but not well understood, pressure-dependence of the structure [2]. Isotropic NTE in this system arises due to the existence of low-energy phonon modes with negative Grüneisen parameters [3]; these modes are also those that soften most rapidly on compression, a view supported by the negative pressure derivative of the bulk modulus, B' , and enhancement of NTE at elevated pressures [4]. Therefore the driving force for clarifying high-pressure phase change behaviour is to allow identification of these key NTE phonon modes, and therefore the mechanism of NTE, in the parent structure. Here we report for the first time the intrinsic high-pressure structure of $\text{Zn}(\text{CN})_2$: at a critical pressure of 1.52 GPa, $\text{Zn}(\text{CN})_2$ ($\text{Pn}3\bar{\text{m}}$) undergoes a phase transition to a lower symmetry (Pbca) structure, $\text{Zn}(\text{CN})_2\text{-II}$ [5]. This transition involves rotations of columns of connected $[\text{Zn}_2(\text{CN})_7]$ tetrahedra pairs that act to “fold up” the structure. These observations therefore shine crucial new light onto the NTE mechanism for this, and other, NTE cyanide framework materials.

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