

Lanthanoid Hexacyanometallates: Hydration Characteristics and Negative Thermal Expansion

S. G. Duyker, C. J. Kepert

School of Chemistry, The University of Sydney, Sydney, NSW, Australia

We present an investigation into the hydration characteristics and thermal expansion properties of the series of isostructural porous cyanide frameworks, the lanthanoid hexacyanometallates, $\text{Ln}^{\text{III}}\text{M}^{\text{III}}(\text{CN})_6 \cdot x\text{H}_2\text{O}$.

These materials form containing both coordinated and non-coordinated water molecules ($x = 4$, $Cmcm$; $x = 5$, $P6_3/mmc$), and the influence of these on the framework structure and properties are of interest. The structural consequences of the transition from a hexagonal pentahydrate phase to a C-centred orthorhombic tetrahydrate phase are discussed and used to explain the appearance of threefold pseudo-merohedral twinning in the tetrahydrates.

The unusual property of negative thermal expansion (NTE, i.e. contraction with heating) was previously reported in dehydrated $\text{ErCo}(\text{CN})_6$.¹ The ionic radius of the lanthanoids decreases by 15% from La to Lu, and the effect of this trend on the framework properties was studied. The uniformity in chemistry across the lanthanoid row was used as an opportunity to decouple the influences of ionic radius and complex stability on thermal expansion behaviour. Variable temperature synchrotron x-ray powder diffraction, with dehydration *in situ*, was used to study the structural changes during dehydration and to identify and measure NTE in several members of the series of dehydrated lanthanoid hexacyanocobaltates. The comparatively minimal variation in the coefficients of thermal expansion (CTEs) for this series contrasts markedly with that seen for the $\text{M}^{\text{II}}\text{Pt}^{\text{IV}}(\text{CN})_6$ Prussian Blue series ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn, Cd}$),² and is attributed to the similarity in coordination chemistry across the lanthanoid series.

(1) Pretsch, T.; Chapman, K. W.; Halder, G. J.; Kepert, C. J. *Chem. Commun.* 2006, 1857.

(2) Chapman, K. W.; Chupas, P. J.; Kepert, C. J. *J. Am. Chem. Soc.* 2006, 128, 7009.