Mapping of the thermal mechanical properties of dicyanometallates

A. J. Corkett[1], A. Grzechnik,[1] K. Friese[1,2]

[1]Jülich Centre for Neutron Science-2 (JCNS-2) Forschungzentrum Jülich GmbH, 52425 Jülich, Germany, [2]Institute of Crystallography, RWTH Aachen University, 52066 Aachen, Germany

a.corkett@fz-juelich.de

Cyanide-based molecular framework materials, featuring corner linked metal centred-polyhedra, frequently display negative thermal expansion (NTE) due to the transverse vibrational motion of the cyanide bridge, as seen in $Cd(CN)_2$ ($\alpha = -33.5$ MK^{-1}) and Prussian blues ($CdPt(CN)_6$, $\alpha = -10.02(11)$ MK^{-1}).[1] Moreover, it has been shown that by replacing diatomic cyanide bridges (M−CN−M) with dicyanometallate linkers (M−CN−A−NC−M, where A = Cu, Ag, Au) one can generate highly flexible interpenetrated networks of corner linked tetrahedra ($M^{II}(A(CN)_2)_2$) and octahedra ($A_3(M(CN)_6)$. Since both of these families adopt hexagonal structures, the thermal expansion in these systems is anisotropic. $Ag_3(Co(CN)_6)$ exhibits positive thermal expansion along *a* ($\alpha_a = +144$ MK^{-1}) and negative thermal expansion along *c* ($\alpha_c = -126$ MK^{-1}) that is an order of magnitude greater than in other crystalline materials.[2] The origin of this 'colossal' response ($\alpha \geq 100$ MK^{-1}) arises directly from the network topology which behaves like a 3D 'garden fence', that can expand in one direction whilst contracting in another with virtually no energy cost.

Here we examine the $LnA_3(CN)_6.3H_2O$ family, which share the same linear dicyanometallate structural motif, and crystallize in hexagonal structures (*P*6_3/*mcm*) featuring H_2O face-capped LnN_6 trigonal prisms that form three identical interpenetrating networks (Figure 1(a)). We have recently shown that it is possible to remove the coordinating water molecules from $LaAu_3(CN)_6.3H_2O$ (*a* = 6.6782(5) Å, *c* = 18.582(1) Å), by thermal treatment under a dynamic vacuum, yielding $LaAu_3(CN)_6$ (*a* = 6.546(1) Å, *c* = 17.430(3) Å) (Figure 1(b)).[3] This desolvation (Figure 1(d)) has a dramatic effect on the thermal expansion coefficients of these phases which go from $\alpha_a = +105$ MK^{-1} and $\alpha_c = -37$ MK^{-1} in $LaAu_3(CN)_6.3H_2O$ to $\alpha_a = +120$ MK^{-1} and $\alpha_c = -91$ MK^{-1} in $LaAu_3(CN)_6$. We then go on to investigate the effect of metallophilicity on this family via Au/Ag substitution on the Kagome lattice (Figure 3(c)) and also explore the compressibility of these phases.

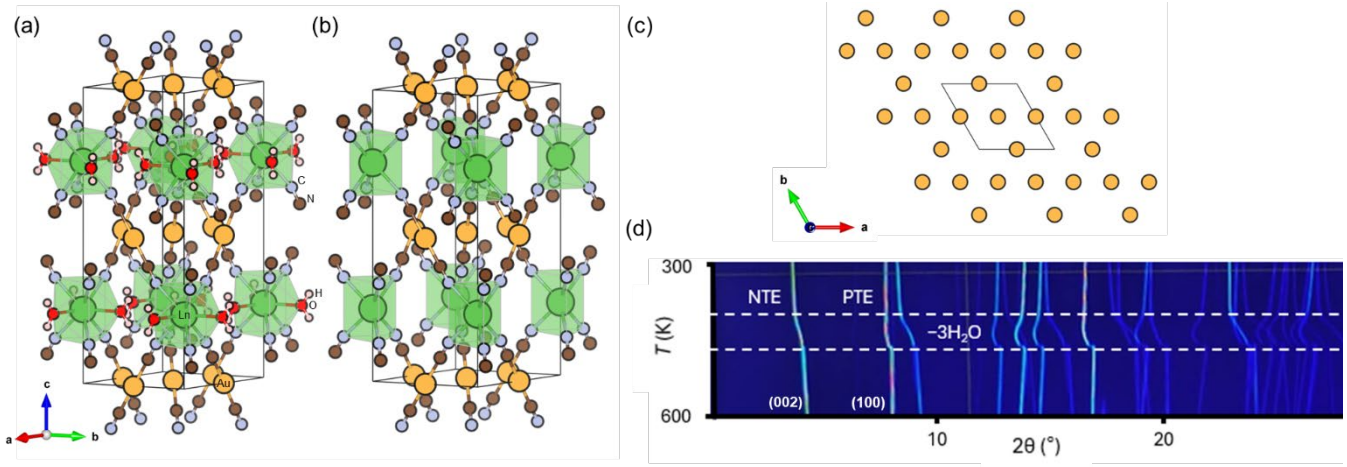

Figure 1. Crystal structure of $LaAu_3(CN)_6.3H_2O$ (a) and $LaAu_3(CN)_6$ (b). Au/Ag Kagome lattice (c). VT PXRD data collected on $LaAu_3(CN)_6.3H_2O$ on the BM01 beamline at the ESRF ($\lambda = 0.6883$ Å) (d).

[1] Fairbank, V. E., Thompson, A. L., Cooper, R. I., Goodwin, A. L. (2012). *Phys. Rev. B* **86**, 104113

[2] Goodwin, A., Calleja, M., Conterio M. J., Dove , M. T., Evans, J. S. O., Keen, D. A., Peters, L., & Tucker, M. G. (2008). *Science* **319**, 794.

[3] Colis, J. C. F., Larochelle, C., Staples, R., Herst-Irmer, R., Patterson, H., (2005). *Dalton Trans*. 675-679