

Negative Thermal Expansion in Metal Cyanides using Variable Temperature Powder Diffraction

Application Note

X-ray Crystallography

Background

Our Gemini S Ultra single-crystal CCD diffractometer (Figure 1) has enabled us to carry out experiments in-house for which we would previously have had to obtain time on central facilities. For example, one research area that we are currently pursuing is the study of negative thermal expansion (NTE), curious thermal behavior in which solids contract rather than expand on heating. Much of the work carried out to date has been on oxide systems, such as $ZrW_2 O_8$ and zeolites, but it has recently become apparent that some cyanides also exhibit NTE and in a number of cases, the effect is larger than in the oxides.



Figure 1. Gemini S Ultra used for these studies (note the dual wavelength, Mo Enhance X-ray source at the front left, Cu high ntensity Enhance Ultra behind).



Authors

Alexander Pohl Ann Chippindale Simon Hibble Department of Chemistry University of Reading UK. Part of this work involves using the Gemini S Ultra CCD diffractometer to follow the evolution of both lattice and atomic parameters as a function of temperature in single-crystal samples. However, it is not possible to prepare single crystals of all the compounds we are studying and so the powder diffraction capability of this machine has proved invaluable. A recent example, presented here, is our study of negative thermal expansion in the cyanides HT-CuCN, AgCN and AuCN, all of which contain infinite $-(M-C\equiv N)-$ chains.

Experimental

Approximately 1 mg of a finely ground mixture of metal cyanide and silicon (internal calibrant) were mounted on a glass fibre using Superglue. Variable-temperature powder X-ray diffraction patterns were collected at intervals of 10 K using the Gemini's high-intensity Enhance Ultra copper radiation source, with either an Agilent Technologies Helijet (Figure 2) (10–100 K) or an Oxford Instruments Cryojet HT (90–490 K). Each image was collected over 240 seconds with a 360 phi rotation and a detector theta offset of 40 degrees giving a 2-theta range 8–72 degrees (Figure 3). The typical variation of powder pattern as a function of temperature is shown in Figure 4.



Figure 2. Agilent Technologies Helijet open flow helium cooling device (10–100 K).



Figure 3. Powder diffraction pattern of HT-CuCN at 10 K and 430 K using Si as an internal standard (denoted by *).



Figure 4. Powder X-ray diffraction patterns of HT-CuCN at 95 K and 430 K. NTE behavior can be seen in the (012) reflection.

Results

Le Bail profile analysis revealed that all the MCN systems show one-dimensional NTE along the c-axis in the direction of the infinite $-(M-C\equiv N)$ - chains, although expansion in the orthogonal ab plane leads to an overall increase in volume (Figure 5). The phenomenon can be rationalised in terms of "skipping-rope" motions of the metal-cyanide chains (Figure 6). Silver cyanide shows particularly interesting behaviour and just above room temperature, the rate of contraction along the c-axis increases. Surprisingly this is not accompanied by an increase in the expansion in the ab-plane and consequently the volume expansion falls to close to zero. Materials exhibiting zero thermal expansion are of interest both academically and technologically, for example where thermomechanical stability is important.



Figure 5. The relative changes with temperature of the lattice parameters and cell volume for HT-CuCN, AgCN and AuCN showing expansion along the a axis and contraction along the c axis.



Figure 6. (a) The structure of MCN (M = Cu, Ag) showing the alignment of $-(M-C \equiv N)$ - chains parallel to the c axis. Note in AuCN the chains are offset along c in a different way.

(b) Metal-cyanide chain at low temperature (LHS) and at higher temperature (RHS) showing how the increased "skipping rope" motion of the chain leads to contraction of the clattice parameter on heating. (Key: M atoms, pink spheres; C/N atoms, cyan spheres).

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