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Zero Thermal Expansion in a Flexible, Stable Framework: Tetramethylammonium Copper(I) Zinc(II) Cyanide

Anthony E. Phillips,[†,‡] Gregory J. Halder,[†,§] Karena W. Chapman,[||] Andrew L. Goodwin,[†,⊥] and Cameron J. Kepert*[,†]

School of Chemistry, The University of Sydney, NSW 2006, Australia, Department of Physics, University of Cambridge, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, U.K., Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

Received August 27, 2009; E-mail: c.kepert@chem.usyd.edu.au

Materials that exhibit zero thermal expansion (ZTE) find uses in applications where precise alignment must be maintained, and thermal shock avoided, over a range of temperatures.[1] Although ZTE can be achieved by composites of ordinary compounds which expand on heating and those which exhibit negative thermal expansion (NTE), this approach leads to strain within the ZTE material, and it is therefore preferable to engineer ZTE behavior at the atomic level within a single material. Compounds known to exhibit near-ZTE over limited temperature ranges include Ag_2O and ReO_3.[2,3] Of the variety of compounds known for their NTE behavior, the family of metal cyanides is of particular interest in engineering new ZTE materials, since these compounds' expansivities can be readily tuned by varying the composition of the frameworks[4,5] and/or guest molecules within them.[6–8] NTE in these compounds has been attributed to low-frequency vibrational modes involving transverse motion of the cyanide bridges, producing a net contraction of the lattice. Thermal expansion in these materials can be tuned by modifying either the framework composition, and thus the flexibility afforded at each metal center,[4] or the guest occupancy, and thus the steric hindrance to the transverse CN modes.[7] The $Cd(CN)_2\cdot CCl_4$ clathrate, which contains CCl_4 guests within a single cristobalite $Cd(CN)_2$ framework, appears promising since its coefficient of thermal expansion $\alpha = \mathrm{d}a/a\mathrm{d}T$ varies substantially with guest occupancy.[8] Unfortunately, this compound is impractical for ZTE applications because the readiness with which the CCl_4 guests desorb makes it difficult to maintain a constant α value.

With the aim of canceling the NTE of a similar host by the permanent inclusion of guests displaying conventional positive thermal expansion, we have investigated the isostructural tetramethylammonium copper(I) zinc(II) cyanide framework, in which the Coulomb force prevents the cations from leaving the anionic host (Figure 1).[9] We here report this framework's structure as a function of temperature, using synchrotron powder and laboratory single-crystal X-ray diffraction in combination with supporting DFT calculations. It demonstrates zero thermal expansion at room temperature, with little variation over a wide temperature range. This behavior results from a combination of transverse CN vibrational modes dampened by the $N(CH_3)_4^+$ guests and considerable flexibility about the Cu^I centers.

The title compound readily forms large, transparent crystals, which above a phase transition at *ca.* 130 K conform to space group $F\bar{4}3m$. The presence of two different metal centers in this space group produces two distinct sets of adamantane pores within the framework, respectively denoted by their 10 nearest metal sites as Cu_4Zn_6 and Zn_4Cu_6, one of which is occupied by the $N(CH_3)_4^+$ ions. In contrast to previous reports of this structure,[9] single-crystal X-ray diffraction data clearly show that the cations occupy exclusively the Cu_4Zn_6 sites (Figure 1). This is supported by DFT modeling using the CASTEP code, which shows that this structure is stabler than the published model by ca. 40 kJ mol^{-1} (see Supporting Information).

The cell parameter *a* was monitored as a function of temperature by single-crystal and powder X-ray diffraction (Figure 2). The data were fit by a straight line below the phase transition and a quintic

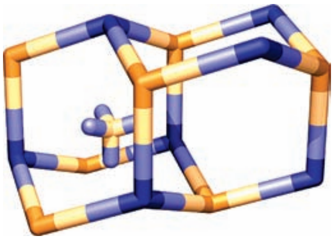

Figure 1. The title compound contains $N(CH_3)_4^+$ ions occupying half of the adamantane pores in the $CuZn(CN)_4^-$ cristobalite framework. Cu atoms are shown in deep blue, Zn in deep yellow, C in light blue, and N in light yellow. For clarity H atoms are omitted.

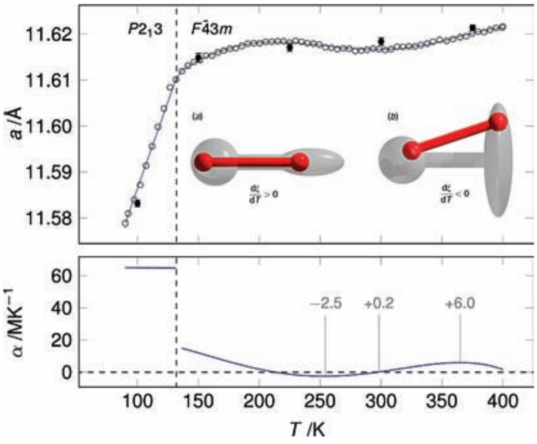

Figure 2. Unit cell parameter (top) and coefficient of thermal expansion (bottom) of $N(CH_3)_4CuZn(CN)_4$ as a function of temperature. Open circles represent powder data, and filled circles single-crystal data. Inset shows two classes of low-energy vibrational mode responsible for the thermal expansivity: (a) distortive, (b) rigid body.

[†] The University of Sydney.
[‡] Department of Physics, University of Cambridge.
[§] Materials Science Division, Argonne National Laboratory.
[||] X-ray Science Division, Argonne National Laboratory.
[⊥] Department of Earth Sciences, University of Cambridge.

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polynomial above, since the thermal expansion is clearly nonlinear in this regime. The fitted curve was used to determine the coefficient of thermal expansion as a function of temperature. Over the temperature range 200−400 K, the compound exhibits near-zero thermal expansion, with a coefficient of thermal expansion of +0.2 MK^{-1} at 25 °C. By comparison, the commercial alloy Super Invar 32-5 has a mean $\alpha = +0.63$ MK^{-1} over the range 218−368 K,[10] while the value for the present compound is +0.67(11) MK^{-1} over the same range.

In Cd(CN)$_2$ and other cyanide frameworks, NTE has been attributed[4,7,8] to transverse *rigid unit modes*, which do not perturb the metal coordination tetrahedra and which hence occur at very low, thermally accessible frequencies.[11] However, other low-frequency modes may also make important contributions to thermal expansivities. In fact, the present compound affords three opportunities to investigate the nature of the vibrational modes responsible for its ZTE. The first is the low-temperature phase, which solves in space group $P2_13$ and appears to result from a second-order phase transition, since the cell parameter varies continuously (Figure 2). This subgroup relation indicates that the transition involves the “freezing-in” of the lowest-frequency X_5 phonon mode, which occurs at the $\langle 100\rangle^*$ points in reciprocal space.[12] In this phase, the framework buckles about and is compressed along the 3-fold axes (see Supporting Information). However, while the ZnN$_4$ tetrahedra show no distortion, with all N−Zn−N angles within experimental error of the ideal 109.5°, the CuC$_4$ tetrahedra are significantly distorted (minimum C−Cu−C angle 107.83(14)°). Moreover, the C atoms which do not lie on 3-fold axes display atomic displacement ellipsoids consistent with further compression of the CuC$_4$ tetrahedra rather than their rotation as a rigid unit.

The second source of information on the relevant phonon modes is analysis of the atomic displacement ellipsoids of the high-temperature phase as a function of temperature.[13] Since the cyanide C and N atoms lie along 3-fold axes, two of the principal axes of their displacement ellipsoids must be equal. The shape of these spheroids can thus be quantified by the aspect ratio ξ, which we define as the ratio of displacement parallel to the bond to that perpendicular to it. The nature of the vibrational modes responsible for the ZTE can be elucidated from the variation in ξ with temperature (Figure 2, inset): an increase, whereby the spheroid becomes more prolate (sausage-shaped), suggests a *distortive* mechanism, whereas a decrease, whereby it becomes more oblate (pancake-shaped), suggests a *rigid-body* mechanism. ξ varies approximately linearly in the temperature range 150−375 K, with $\mathrm{d}\xi/\mathrm{d}T = +0.36(6)$ kK^{-1} for the C atoms and −0.54(16) kK^{-1} for the N atoms. Third and finally, considering the crystallographic bond distances of the high-temperature phase as a function of temperature shows the Zn−N distance appearing to contract ($\mathrm{d}l/l\mathrm{d}T = -23(3)$ MK^{-1}), as expected if each ZnN$_4$ tetrahedron rotates as a unit, while the Cu−C distance expands (average $\mathrm{d}l/l\mathrm{d}T = +65(3)$ MK^{-1}; see Supporting Information).

Each of these observations demonstrates that low-frequency modes distort the CuC$_4$ tetrahedra significantly while leaving the ZnN$_4$ tetrahedra approximately rigid. Similar behavior occurs in Cu$_2$O, which has the inverse structure, with Cu ions bridging O-centered tetrahedra: low-frequency modes which distort the Cu$^{\mathrm{I}}_4$O tetrahedra are important contributors to this system’s NTE.[3] Distortion of the CuC$_4$ tetrahedra in the present system may similarly play an important role in its ZTE: indeed, the apparent Cu−C bond lengths increase with temperature precisely when α is negative, and vice versa (see Supporting Information). The precise effects on the expansivity of the distortive and rigid-body modes, however, are not easily decoupled.

These results demonstrate that the NTE observed in cristobalite-type cyanide frameworks can be converted to zero thermal expansion by the inclusion of ionic guests within a charged host. Since the ionic guests cannot be removed, unlike their neutral analogues in the Cd(CN)$_2$ framework, they can be relied upon to maintain zero thermal expansion over many heating cycles. Some of the low-frequency modes responsible for the anomalous thermal expansion involve the distortion of coordination tetrahedra: we propose that this effect is of more general importance in NTE materials than has been widely recognized and intend to examine it further. Nevertheless it is the existence of low-energy NTE modes, whatever their nature, coupled with the expansion of the electrostatically trapped guests, that provides stable near-zero thermal expansion over a wide temperature range in this novel material.

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Supporting Information Available: Synthetic method; experimental method and crystallographic data for the high- and low-temperature phases; details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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