PHASE TRANSITIONS IN HYDROGEN-BONDED INORGANIC ACIDS. S.M. Haile, P. Calkins, S. Fu, S. Faulk and G. Stine, Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195

A number of solid acid sulfates and phosphates exhibit ferroelectric transitions at low temperatures and superprotonic transitions at elevated temperatures. In particular, CsH2PO4 undergoes a ferroelectric transition at 170K, whereas CsHSO4 undergoes a superprotonic transition at 417K. While the structural features that lead to ferroelectricity in CsH2PO4 and not in CsHSO4 are fairly well understood, the same cannot be said of superprotonic transitions. In this work we have investigated phase transitions in a number of CsHSO4-CsH2PO4 compounds. Selected models describing ferroelectric transitions are examined with respect to the new compounds. Cs3(HSO4)2(H2PO4) and Cs2(HSO4)3(H2PO4)2, both of which exhibit ferroelectric transitions. In both, low temperature ferroelectricity is expected based on the presence of locally disordered hydrogen bonds in the room temperature structures. With respect to high temperature transformations, we propose that, in contrast, superprotonic transitions are driven by global features of the hydrogen bonded network. Specifically, the compounds CsHSO4, Cs3(HSO4)2(H2PO4) and Cs2(HSO4)3(H2PO4)2, all of which undergo superprotonic transitions, all contain some oxygen atoms that do not participate in hydrogen bonding. At elevated temperatures, entropy considerations drive the compounds to a state in which all oxygen atoms are chemically, if not crystallographically equivalent. As the number of protons is not sufficient to satisfy all the potential hydrogen bonds, the only way in which all oxygen atoms can participate in hydrogen bonding is via the introduction of partial occupancies, either on oxygen sites or proton sites or both. It is precisely this state of disorder that leads to a highly conducting state. Relevant details of the structures of these new compounds supporting the present hypothesis are described.

STRUCTURAL TRANSFORMATION OF A [Cd(CN)3]In FRAMEWORK. Michaelle J. Hardie, Brendan F. Abrahams, Bernard F. Hoskins, Richard Robson and G. A. Williams, School of Chemistry, University of Melbourne, Parville 3052, Victoria, Australia.

The cadmium cyanide - alcohol clathrate Cd(CN)2.2H2O.BuOH can undergo a remarkable single crystal to single crystal transformation involving extensive topological change. The structural chemistry of cadmium cyanide derivatives is diverse and a number of geometrically and topologically distinct 3D frameworks structures are known. The structure of Cd(CN)2.2H2O.BuOH is a honeycomb-like [Cd(CN)3]In framework with solvent t-butanol molecules occupying the hexagonal-shaped channels. The t-butanol molecules can be displaced by other volatile organic species and this solvent-exchange is accompanied by a reorganisation of the [Cd(CN)3]In framework to a single diamondoid network. The crystals retain their clarity, external morphology and single nature.


TWO NEW PSEUDO-ISOTYPIC ZIRCONIUM NITRILOTRIACETATES OF GUANIDINIUM AND NICKEL. E. Haussühl, G. Giester and E. Tillmanns, Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 14, A-1090 Wien, Austria

Crystals of nitrilotriacetic acid, H3NTA (NTA"=N(CH2COO)3) and several of its salts show surprisingly large nonlinear optical effects. Similar strong polar effects were detected in crystals of the type X2Zr(NTA)2y H2O. Large single crystals of Nizr(NTA)2 (H2O) (I) and (CNH3)2Zr(NTA)2 H2O (II) have been obtained from aqueous solutions by controlled cooling from 296 to 291 K over a period of about two months. The raw materials were produced by reacting the carbonates of guanidinium and nickel, respectively, with the stoichiometric quantities of an aqueous solution of ZrCl4 and nitrilotriacetic acid.

Crystals of the two species exhibit a similar morphology (point symmetry 222). Their crystal structures (space group C2221, Z = 4) show close relationships. Lattice constants at 293 K are:

(I) a = 10.009 Å, b = 20.710 Å, c = 11.514 Å and
(II) a = 11.279 Å, b = 20.258 Å, c = 10.346 Å

The tensors of thermal expansion, dielectricity, piezoelectricity and elasticity determined with the use of large single crystals show strong anisotropy in both species. Piezoelectric effects more than 25 times larger than d11 of α-quartz are observed. (I) undergoes phase transitions between 287.5 and 289.6 K which appear to be of the third order.

Isolated Zr(NTA)2y molecules are similarly arranged in both structures and form sheets parallel to the plane (010). The large cations guanidinium and nickel occupy positions between these sheets with one octahedral Ni2+(H2O)6 complex in a special position in (I) replacing two guanidinium+ ions in a general position in (II). Hydrogen bonds are formed between Ni(H2O)6 octahedra in (I) or guanidinium ions and water molecules in (II), respectively, and oxygen atoms of the acetate groups.

POLYMORPHISM OF TH3PO4 AND TDPPO4. G. Heger1, S. Rios2, W. Paulus2, L. Cousse2, M. Quillichini2, M. Becker1, J. Gillemann1, E. Haussuhl1, G. Giester1, Institute for Crystallography, University of New South Wales, Sydney, Australia; 1 Institute for Crystallography, University of New South Wales, Sydney, Australia.

The crystal structures of TH3PO4 (TDP) and TDPPO4 (DTDP) are principally characterized by hydrogen bonded PO4 groups which form a double-layer arrangement instead of the 3 dim. network known for the related KH2PO4 (KDP) phases. We have reexamined the crystal structures and phase transitions of TDP and DTDP as a function of temperature by X-ray and neutron diffraction on powders and single crystals in order to clarify contradictions in the literature[1]. The gradual ordering of the protons/deuterons in the hydrogen bonds leads to two different branches of symmetrically distinct phases. The common orthorhombic high temperature structure of space group type P212121/n with Z = 4 shows a dynamical hydrogen disorder in a double-well potential along all the O-H-D-O bonds. The two monoclinic structures at room temperature with partial hydrogen ordering (TDP: P21/c, Z = 4; DTDP: P21/c, Z = 8) differ mainly due to the orientation of their remaining two-fold axes. Therefore, the almost equal phase transition temperatures for TDP (Tm = 350 K) and DTDP (Tm = 357 K) cannot be interpreted in terms of an isotope effect. For TDP-III below 230 K, there is a triclinic low temperature phase (P1, Z = 8) with complete H ordering. Since all of the polymorphous TDP/ DTDP phases are centrosymmetric ferroelectric behaviour is ruled out.