

**PS11.05.09 PHASE TRANSITIONS IN HYDROGEN-BONDED INORGANIC ACIDS.** S.M. Haile, P. Calkins, S. Fu, S. Faulk and G. Stanoff, 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,  $\text{CsH}_2\text{PO}_4$  undergoes a ferroelectric transition at 170K, whereas  $\text{CsHSO}_4$  undergoes a superprotonic transition at 417K. While the structural features that lead to ferroelectricity in  $\text{CsH}_2\text{PO}_4$  and not in  $\text{CsHSO}_4$  are fairly well-understood, the same cannot be said of superprotonic phase transitions. In this work we have investigated phase transitions in a number of  $\text{CsHSO}_4$ - $\text{CsH}_2\text{PO}_4$  compounds. Selected models describing ferroelectric transitions are examined with respect to the new compounds,  $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_5(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_2$ , 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  $\text{CsHSO}_4$ ,  $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$  and  $\text{Cs}_5(\text{HSO}_4)_3(\text{H}_2\text{PO}_4)_2$ , 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.

**PS11.05.10 STRUCTURAL TRANSFORMATION OF A  $[\text{Cd}(\text{CN})_2]_n$  FRAMEWORK.** Michael 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  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{BuOH}$  can undergo a remarkable single crystal to single crystal transformation involving extensive topological change<sup>1</sup>. The structural chemistry of cadmium cyanide derivatives is diverse and a number of geometrically and topologically distinct 3D frameworks structures are known<sup>2</sup>. The structure of  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{BuOH}$  is a honeycomb-like  $[\text{Cd}(\text{CN})_2]_n$  framework with solvent t-butanol molecules occupying the hexagonal-shaped channels<sup>3</sup>. The t-butanol molecules can be displaced by other volatile organic species and this solvent-exchange is accompanied by a reorganisation of the  $[\text{Cd}(\text{CN})_2]_n$  framework to a single diamondoid network. The crystals retain their clarity, external morphology and single nature.

1. B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and G. A. Williams, *J. Am. Chem. Soc.* 1992, 114, 10641
2. For example (a) T. Kitazawa, T. Kikuyama, M. Takahashi and M. Takeda, *J. Chem. Soc., Dalton Trans.* 1994, 2933; (b) T. Kitazawa, S. Nishikiori and T. Iwamoto, *J. Chem. Soc., Dalton Trans.* 1994, 3695.
3. B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc.; Chem. Commun.* 1990, 60.

**PS11.05.12 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,  $\text{H}_3\text{NTA}'$  ( $\text{NTA}' = \text{N}(\text{CH}_2\text{COO})_3$ ) and several of its salts show surprisingly large nonlinear optical effects. Similar strong polar effects were detected in crystals of the type  $\text{X}_2\text{Zr}(\text{NTA}')_2 \cdot y\text{H}_2\text{O}$ . Large single crystals of  $\text{NiZr}(\text{NTA}')_2 \cdot 8\text{H}_2\text{O}$  (I) and  $(\text{C}(\text{NH}_2)_3)_2\text{Zr}(\text{NTA}')_2 \cdot \text{H}_2\text{O}$  (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  $\text{ZrCl}_4$  and nitrilotriacetic acid.

Crystals of the two species exhibit a similar morphology (point symmetry 222). Their crystal structures (space group  $\text{C}222_1$ ,  $Z = 4$ ) show close relationships. Lattice constants at 293 K are:

$$\begin{array}{lll} \text{(I)} & a = 10.009 \text{ \AA}, & b = 20.710 \text{ \AA}, & c = 11.514 \text{ \AA} \\ \text{(II)} & a = 11.279 \text{ \AA}, & b = 20.258 \text{ \AA}, & c = 10.346 \text{ \AA} \end{array}$$

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  $d_{111}$  of  $\alpha$ -quartz are observed. (II) undergoes phase transitions between 287.5 and 289.6 K which appear to be of the third order.

Isolated  $\text{Zr}(\text{NTA}')_2$  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  $\text{Ni}^{2+}(\text{H}_2\text{O})_6$  complex in a special position in (I) replacing two guanidinium<sup>1+</sup> ions in a general position in (II). Hydrogen bonds are formed between  $\text{Ni}(\text{H}_2\text{O})_6$  octahedra in (I) or guanidinium ions and water molecules in (II), respectively, and oxygen atoms of the acetate groups.

**PS11.05.13 POLYMORPHISM OF  $\text{TiH}_2\text{PO}_4$  AND  $\text{TiD}_2\text{PO}_4$ .** G. Heger<sup>1</sup>, S. Rios<sup>2</sup>, W. Paulus<sup>1,2</sup>, A. Cousson<sup>2</sup>, M. Quilichini<sup>2</sup>, M. Becker<sup>1</sup>, J. Glinnemann<sup>1</sup>. <sup>1</sup>RWTH Aachen, Institut für Kristallographie, D-52056 Aachen, Germany; <sup>2</sup>Laboratoire Léon Brillouin, CE Saclay, F-91191 Gif-sur-Yvette, France

The crystal structures of  $\text{TiH}_2\text{PO}_4$  (TDP) and  $\text{TiD}_2\text{PO}_4$  (DTDP) are principally characterized by hydrogen bonded  $\text{PO}_4$  groups which form a double-layer arrangement instead of the 3 dim. network known for the related  $\text{KH}_2\text{PO}_4$  (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  $\text{P}2_1/\text{c}2_1/\text{a}2_1/n$  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-II:  $\text{P}12_1/\text{a}1$ ,  $Z = 4$ ; DTDP- $\gamma$ :  $\text{P}112_1/\text{a}$ ,  $Z = 8$ ) differ mainly due to the orientation of their remaining two-fold axes. Therefore, the almost equal phase transition temperatures for TDP ( $T_{\text{I-II}} = 350 \text{ K}$ ) and DTDP ( $T_{\text{I-II}} = 357 \text{ K}$ ) cannot be interpreted in terms of an isotope effect. For TDP-III below 230 K, there is a triclinic low temperature phase (P 1,  $Z = 8$ ) with complete H ordering. Since all of the polymorphous TDP/DTDP phases are centrosymmetric ferroelectric behaviour is ruled out. For  $\gamma$ -DTDP antiferroelectricity was found [2].

[1] S.Rios, W. Paulus, A. Cousson, M. Quilichini, G. Heger, N. Le Calvé and B. Pasquier, *J. Phys. I France* 5, 763 (1995)

[2] N. Yasuda, S. Fujimoto and T. Asano, *Phys. Lett. A* 76, 174 (1980)