

Engineering, North Carolina State University, Box 7905, 911 Partners Way, Raleigh, NC 27695, E-mail: vyoung@umn.edu

Low-melting organic salts often exhibit complex temperature-dependent properties. Below melting temperatures these are best described as crystalline materials with liquid-like properties where some or all of the cations and/or anions are disordered. At yet lower temperatures, as monitored by DSC, these undergo stepwise phase transitions to ordered phases. Many of these have intermediate phases with both ordered and/or disordered species. These cascades of phase transitions often produce the lowest temperature phases with pseudo-symmetric, high- Z' structures that are often twinned by non-merohedry. For example, the material $[\text{N}(\text{CH}_3)_4][\text{IM14}]$, where IM14 is $\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$, exhibits two first-order phase transitions by DSC at 168 K and 193 K before melting at 390 K. Phase I is found in space group $P2_1/m$ where the IM14 anion is disordered over the crystallographic mirror and the $[\text{N}(\text{CH}_3)_4]$ is bisected by it. In Phase II the unit cell doubles as the crystallographic mirror transforms to a glide plane as the space group $P2_1/n$ emerges. The IM14 anion is disordered in both Phases I and II, but not in III. The space group for Phase III is $P2_1/n$, as is Phase II, however the order/disorder phase transition causes a major reconstruction of the contents and the a - and c -axes. The inter-phase symmetry modifications of this and several other low-melting organic salts with multiple phase transitions will be the focus of this paper.

Keywords: low-melting compounds, phase transitions, organic inorganic materials

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Intrinsic ferroelectric instability in $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ revealed by changing B-site randomness

Kenji Ohwada

Japan Atomic Energy Agency / Japan, Quantum Beam Science Directorate, 1-1-1 Koto, Sayo, Sayo, Hyogo, 679-5148, Japan, E-mail: ohwada@spring8.or.jp

Antiferroelectric (AFE), ferroelectric (FE) or relaxor states can appear in $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PIN) depending upon the perovskite B-site randomness. We studied the effects of this randomness on the dynamics of PIN by high resolution inelastic x-ray scattering using ordered PIN (AFE) and disordered PIN (relaxor) single crystals. We have found a clear softening of a transverse optic mode at the Gamma-point in both the samples, indicating a robust and intrinsic ferroelectric dynamical correlation regardless of the actual ground state. We believe that the correlation results in a FE instability mode, which gives yield to the FE and relaxor states. We interpret that AFE is stabilized only when In and Nb ions are spatially ordered enough to overwhelm the FE instability. As the B-site randomness becomes larger, AFE is suppressed and the hidden FE state starts appearing. Ultimately, the randomness begins to predominate over the development of FE regions and blocks a long range FE order, which we believe yields polar nanoregions resulting in relaxor behaviors. This work was performed in collaboration with Prof. K. Hirota (Osaka Univ.), Dr. T. Fukuda (JAEA), Dr. S. Tsutsui (JASRI/Spring-8), Dr. A. Q. R. Baron (RIKEN), Dr. J. Mizuki (JAEA), Prof. H. Terauchi (Kwansei Gakuin Univ.), Prof. H. Ohwa (Gifu Univ.) and Prof. N. Yasuda (Gifu Univ.).

Keywords: relaxor, ferroelectrics, inelastic x-ray scattering

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A new conformation of *meso*-tetraphenylporphyrin free-base structure

Chuttree Phurat¹, Narongsak Chaichit², Nongnuj Muangsin¹

¹Research Centre for Bioorganic Chemistry, Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai, Bangkok, 10330, Thailand, ²Department of Physics, Faculty of Science and Technology, Thammasart University, Patumthani, 12120, Thailand, E-mail: freshytulip@yahoo.com

The new conformation of *meso*-tetraphenylporphyrin was prepared accidentally. It is named T1. T1 has been characterized by a three-dimensional X-ray structure determination and refined by least-squares methods on a R value of 0.0451 based on F . The complex crystallizes in the triclinic space group $P-1$, with $a=6.436$, $b=10.477$, and $c=12.416$ Å. There are two molecules in the unit cell and no solvent molecules in lattice. The out-of-plane distortions of porphyrins are characterized by displacements along the lowest-frequency out-of-plane normal coordinates of macrocycle and comparison with other porphyrins. It shows some differences, especially the dihedral angle between *meso*-substituents and pyrrole rings.

Keywords: porphyrins, *meso*-tetraphenylporphyrin, porphyrin conformations

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Probability density analysis for mobile ions in a hollandite superstructure

Yuichi Michiue

National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan, E-mail: MICHIE.Yuichi@nims.go.jp

Ordering schemes for guest ions and the host structure in a hollandite superstructure of $\text{K}_x(\text{Mg,Sb})_8\text{O}_{16}$ ($x=1.76$) were investigated by a single-crystal X-ray diffraction technique. Superlattice formation is primarily attributed to the Mg/Sb occupational modulation in the host structure. Two types of the cavity are linearly connected forming a one-dimensional tunnel, where K ions are accommodated. Parts of K ions deviate from the cavity center along the tunnel direction. Probability densities of K ions in the two cavities are different from each other, which seems to have arisen from the Mg/Sb modulation. Transport property of K ions was investigated by considering additional constraint conditions in least-squares refinements so that the average structure obtained from the refinement was consistent with possible microscopic pictures. One-particle potential along the conduction path was drawn from probability density functions for specific K ions concerning the hopping process between neighboring cavities. Energy barriers in three types of K hopping processes, 62, 90, 110 meV, were estimated using harmonic atomic displacement parameters (ADPs), which were reduced to 45, 79, and 96 meV in the anharmonic ADP model. The values are generally consistent with results from impedance measurements in microwave frequencies reported so far.

Keywords: hollandite, superstructures, ion transport