

MS.30.1*Acta Cryst.* (2008). A64, C59**Where are Nature's missing structures?**

Gus LW Hart

Brigham Young University, Physics and Astronomy, N249 Eyring Science Center, Provo, UT, 84602, USA, E-mail: gus.hart@gmail.com

Our society's environmental and economic progress depends on the development of high-performance materials such as lightweight alloys, high-energy-density battery materials, recyclable motor vehicle and building components, and energy-efficient lighting. Meeting these needs requires us to understand the central role of crystal structure in a material's properties. Despite more than 50 years of progress in first-principles calculations, it is still impossible in most materials to infer ground-state properties purely from a knowledge of their atomic components--a situation described as 'scandalous' in the well-known essay by Maddox. Many methods attempt to predict crystal structures and compound stability, but here I take a different tack--to infer the existence of structures on the basis of combinatorics and geometric simplicity. The method identifies 'least random' structures, for which the energy is an extremum (maximum or minimum). Although the key to the generic nature of the approach is energy minimization, the extrema are found in a chemistry-independent way.

Keywords: structure prediction, hypothetical structures, alloys

MS.30.2*Acta Cryst.* (2008). A64, C59**High-voltage cathodes for Li-ion batteries: Metallophosphoolivines and manganese-based spinels**Natalia N. Bramnik^{1,2}, Kristian Nikolowski^{1,2}, Aiswarya Bhaskar^{1,2}, Carsten Baehtz³, Dmytro Trots³, Anatoliy Senyshin¹, Hartmut Fuess¹, Helmut Ehrenberg^{1,2}

¹Darmstadt University of Technology, Institute for Materials Science, Petersenstr. 23, Darmstadt, Germany, 64287, Germany, ²IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, Dresden, 01069, Germany, ³HASYLAB/DESY, Notkestr. 85, Hamburg, 22603, Germany, E-mail: bramnik@tu-darmstadt.de

The use of high voltage cathode materials operating at voltages close to 5V vs metallic Li is an effective way to increase the energy density of rechargeable batteries. Among possible candidates, metallophosphates with olivine structure LiMPO_4 ($M = \text{Co}, \text{Ni}$) and substituted spinels with general formula $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$ ($M = \text{Co}, \text{Ni}, \text{Cr}$) attracted much attention in the last years. These compounds will be discussed here in respect to their delithiation mechanism during electrochemical charge-discharge and strategy for materials optimisation. The delithiation of LiCoPO_4 leads to the formation of lithium-deficient phases Li_xCoPO_4 with $x = 0.6$ and $x = 0$ as determined by powder neutron diffraction. Temperature dependent synchrotron diffraction revealed a low thermal stability of the delithiated phases, which decompose upon slight heating with accompanied oxygen release. This is in contrast to LiFePO_4 , which is the most stable cathode material at present and where both the fully lithiated and the delithiated compositions occur naturally as the minerals triphylite and heterosite, respectively. The influence of a partial substitution of Co with Fe, Mn, Ni on the thermal stability and the mechanism of lithium extraction-insertion were studied by in situ synchrotron diffraction and DTA/TG. Another optimization strategy is discussed for the substituted spinel prepared by sol-gel method. To improve cycling stability, different coatings procedures were

applied. The quality of the coatings were characterised by XPS and TEM analysis. The cycling behaviour and rate capability for different coatings will be compared and discussed.

Keywords: *in situ* powder diffraction, battery materials, solid-state electrochemistry

MS.30.3*Acta Cryst.* (2008). A64, C59**Towards a better understanding of atomic arrangements in nano-minerals**

John B Parise, Marc F Michel

Stony Brook University, Ess Building RM 238, Stony brook, NY, 11733, USA, E-mail: john.parise@sunysb.edu

Nano-crystalline minerals are important components of soil [1], biogeochemical processes and are vital components of several elemental cycles, such as the sulfur cycle on Earth and probably mars [2]. Derivation of testable structural models for nano-minerals requires a total scattering approach - measurement of elastic coherent diffuse scattering in the presence of dominant inelastic background and broad Bragg scattering peaks. High energy X-rays (> 60 keV) and spallation neutrons provide data to high Q and derivation of quantitative pair distribution functions (PDF) of sufficient resolution to observe subtle deviations that are crucial to distinguishing closely related structure models, and whether particular nano-crystalline materials are indeed single phase. This is already impacting studies of glasses, melts and nano-crystalline materials. Other extreme conditions such as fast kinetic studies of nano-crystalline materials growth in capsids such as ferritin may also be possible. In the past few years we have made considerable progress in defining several nano-materials: n-FeS is shown to be mackinawite-related and undergoes transitions to new phases at high pressure. The search for a consistent description of the atomic arrangement in iron oxide hydroxides indicates ferrihydrite is adequately described as a single phase, with a closely related structure models appropriate for description of this material in the environment and in the core of the protein ferritin. We acknowledge the considerable contributions to this work of L. Ehm, R Reeder, B. Phillips and C. Tarabrela, S.A. Antao, P.L. Lee, C.D. Martin, P. Chupas, K. Chapman, and S. Shastri [1] Rice et al *Adv Inorg Biochem* 5, 39 (1983) [2] Berner *Early Diagenesis*. Princeton University Press, pp. 26 (1980)

Keywords: nano-material, total-scattering, PDF

MS.30.4*Acta Cryst.* (2008). A64, C59-60**Kesterite - an alternative absorber material for thin film solar cells**Susan Schorr¹, Michael Tovar², Alfons Weber³, Hanna Krauth³, Veijo Honkimaki⁴, Hans-Werner Schock³

¹Free University Berlin, Geosciences, Malteserstr. 74-100, Berlin, Berlin, D-12249, Germany, ²Hahn-Meitner-Institut Berlin, Dep. Structural Research, Glienicker Str. 100, D-14109 Berlin, Germany, ³Hahn-Meitner-Institut Berlin, Dep. Solar Energy Research, Glienicker Str. 100, D-14109 Berlin, Germany, ⁴ESRF, 6 Rue Jules Horowitz, BP 220, 38043 Grenoble Cedex, France, E-mail: susan.schorr@fu-berlin.de

Photovoltaics is one of the most easily implementable renewable energy source. Highly efficient thin film solar cells based on

compound semiconductors such as Cu(In,Ga)Se₂ as absorbers. Since the availability of indium is an object of concern regarding solar cell large scale production, its replacement with Zn and Sn is beneficial in this sense. The alternative compound kesterite (Cu₂ZnSnS₄) has promising characteristic optical properties. The structure of kesterite consists of a *ccp* array of sulfur atoms, with metal atoms occupying one half of the tetrahedral voids. In literature an ordered distribution of Cu⁺, Zn²⁺ and Sn⁴⁺ is described. A disordered distribution may cause site defects and hence influences the electronic properties of the material. Thus the degree of cation order plays a crucial role and was therefore the focus of the presented investigations. Combined neutron and X-ray diffraction experiments revealed that the degree of cation order depends on the thermal history of the kesterite. In quenched samples Cu⁺ and Zn²⁺ are disordered, whereas in samples where a controlled cooling was applied, a certain degree of cation order is achieved. To shed more light into the formation process of kesterite, *in-situ* high temperature synchrotron X-ray diffraction experiments on stoichiometric mixtures of binary and ternary sulfides were performed. Structural phase transitions and formation of new phases, resulting in kesterite formation, can be observed in detail by mapping the diffractograms and Rietveld analysis. The variation of the kesterite lattice parameter with temperature, especially during the kesterite nascency, indicates changes in the cation distribution. Completing the presentation, first promising results of kesterite thin film solar cells will be shown.

Keywords: solar cells, cation distribution, *in-situ* high temperature diffraction

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Phase composition of mineral trioxide aggregate and its role on properties as biomaterial cement

Lauro Bucio¹, Irma Araceli Belio-Reyes², Esther Cruz-Chavez²

¹Instituto de Física, Universidad Nacional Autónoma de México, Estado Solido, Circuito de la Investigación Científica s/n, Ciudad Universitaria, México, Distrito Federal, 01000, México, ²Facultad de Odontología, Universidad Autónoma de Sinaloa, Culiacán, Sinaloa, México, E-mail : bucio@fisica.unam.mx

Quantitative phase analysis of ProRoot Mineral Trioxide Aggregate (MTA) was performed applying the Rietveld method to its X-ray powder diffraction data (XRD). Six crystalline phases were identified as constituents: bismuth oxide, tricalcium silicate, dicalcium silicate, calcium dialuminate, calcium sulphate dehydrated, and tricalcium aluminate. In order to limit the entries for phase identification, chemical analysis by Energy Dispersive Spectrometry (EDS), Rutherford Backscattering Spectrometry (RBS) and Particle induced X-ray emission (PIXE) were used and was found in agreement with the phases identified by XRD. As cement for use in dentistry, MTA has been investigated as root-end filling and as sealing material in periapical dental surgeries, showing good response in the forming tissue. In cases of open apices, MTA seems to act in cell reactions stimulating the regeneration of biological tissue. The action of MTA can be explained on the basis that when tricalcium and dicalcium silicates are hydrated, they produce calcium silicate hydrate gel (CSH) and calcium hydroxide. The last acts as alkaline reservoir, keeping the pH at higher values creating an unfavourable environment for bacteria to survive. On the other hand, the release of calcium atoms from the cement in adjacent tissues stimulate hard tissue deposition.

Keywords: biomaterial, mineral trioxide aggregate, biocement

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Switching magnetic molecular materials

Eugenio Coronado, Miguel Clemente-Leon, Mauricio Lopez-Jorda, Francisco M. Romero

University of Valencia - Instituto de Ciencia Molecular, Department of Inorganic Chemistry, Polígono La Coma, s/n, Paterna, Valencia, 46980, Spain, E-mail : eugenio.coronado@uv.es

The field of functional molecular materials has seen a very rapid progress since the discovery of a variety of cooperative solid-state properties such as conductivity and superconductivity, non-linear optics, and ferromagnetism. Currently, one of the most appealing aims in this field is that of creating complex materials in which these cooperative properties can be tuned by external stimuli (light, temperature, pressure). One can imagine two possible approaches to reach this goal: a) The two-network approach, which is based on materials formed by two molecular networks. In this case the magnetic or conducting properties of one of the two networks are influenced by the structural changes induced in the crystal lattice by the second network, which is formed by a switchable molecule; b) The one-network approach, which is based on materials formed by a single magnetic or conducting molecule-based network. In this case the material contains in this network an electroactive or photoactive molecular component that can switch when the external perturbation is applied. Here we will show two examples that illustrate this concept in molecular magnetism. The first one is provided by two-network materials formed by bimetallic oxalato-based magnets and spin-crossover Fe(II) and Fe(III) complexes, while the second one is provided by one-network Prussian-Blue materials that undergo magnetic switching when an external pressure is applied.

Keywords: materials chemistry, magnets, molecular magnets

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Structures and physical properties of single-component molecular metals

Akiko Kobayashi

Nihon University, College of Humanities and Sciences, Sakurajosui 3-25-54, Setagaya -ku, Tokyo, 156-8550, Japan, E-mail : akoba@chs.nihon-u.ac.jp

In contrast to typical inorganic metals composed of single elements, such as sodium and copper, all of the molecular metals developed until recently had been consisted of more than two kinds of molecules. In 2001, we developed the first single-component molecular metal with extended-TTF ligands, [Ni(tmdt)₂] (tmdt = tri methylenetetrafulvalenedithiolate) exhibiting metallic behavior down to very low temperature. A direct experimental evidence for the three-dimensional electron and hole Fermi surfaces in [Ni(tmdt)₂] was obtained by detecting the quantum oscillations in magnetization (de Haas-van Alphen (dHvA) effect) at low temperature under very high magnetic field. The neutral bis(dithiolato)gold complex [Au(tmdt)₂] is isostructure to [Ni(tmdt)₂]. The ESR, ¹H NMR, μ SR and magnetic susceptibility measurements revealed that [Au(tmdt)₂] has the antiferromagnetic phase transition around 110 K. The single crystal resistivity measurement of [Au(tmdt)₂] using extremely small crystal of ca. 30 μ m showed the system to be metallic down to 4 K. All these data shows that [Au(tmdt)₂] is the first AF molecular metal with T_N above 100 K and metal electron and magnetic order coexist down to low temperature. Recently we have prepared [Pd(tmdt)₂] and [Pt(tmdt)₂] whose crystal structures were almost the same with those