

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

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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<sup>1,2</sup>, Kristian Nikolowski<sup>1,2</sup>, Aiswarya Bhaskar<sup>1,2</sup>, Carsten Baehtz<sup>3</sup>, Dmytro Trots<sup>3</sup>, Anatoliy Senyshin<sup>1</sup>, Hartmut Fuess<sup>1</sup>, Helmut Ehrenberg<sup>1,2</sup>

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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  $\text{LiMPO}_4$  ( $M = \text{Co}, \text{Ni}$ ) 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  $\text{LiCoPO}_4$  leads to the formation of lithium-deficient phases  $\text{Li}_x\text{CoPO}_4$  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  $\text{LiFePO}_4$ , 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**

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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. Tarabrella, 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 Schorr<sup>1</sup>, Michael Tovar<sup>2</sup>, Alfons Weber<sup>3</sup>, Hanna Krauth<sup>3</sup>, Veijo Honkimaki<sup>4</sup>, Hans-Werner Schock<sup>3</sup>

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