

Poster Sessions

The first borohydrides with both mixed cations and anions, $\text{LiCe}(\text{BH}_4)_3\text{Cl}$ has recently been synthesized from LiBH_4 and CeCl_3 . The product, which has earlier been mistaken for $\text{Ce}(\text{BH}_4)_3$ [2,3], is structurally characterized by combined PXD and PND. Li is found in two very different chemical environments; one which resembles LiCl and one similar to LiBH_4 . The compound gives off 6 wt% of almost pure hydrogen gas around 250°C. Preliminary results show limited reversibility due to formation of CeH_x .

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[1] H.W. Brinks, A. Fossdal, B.C. Hauback, *Journal of Physical Chemistry C* **2008**, *112*, 5658-5661. [2] F.C. Gennari, M.R. Esquivel, *J. Alloys Comp.* **2009**, *485*, L47-L51. [3] B.J. Zhang, B.H. Liu, Z.P. Li, *J. Alloys Comp.* **2011**, *509*, 751-757.

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Single crystal neutron diffraction study on $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$
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In this work, we present a crystal structure investigation on $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$ by single crystal neutron diffraction. The title compound, which is isostructural to TlH_2PO_4 (TDP), crystallizes in the monoclinic space group $\text{P}12_1/a1$ with $a = 14.428(1) \text{ \AA}$, $b = 4.543(5) \text{ \AA}$, $c = 6.400(9) \text{ \AA}$ and $\beta = 91.77(9)^\circ$. TDP is characterized by a two-dimensional network of hydrogen bonds. Although the ionic radii of Tl^+ and Rb^+ are almost same (1.47 Å), the crystal structures of RbH_2PO_4 (RDP) and TDP are different from each other. The disordered H-distributions have been investigated in detail [1,2]. Highly perfect mixed crystals were grown from aqueous solution. Diffraction data at room temperature were measured up to $(\sin\theta/\lambda) = 0.827 \text{ \AA}^{-1}$ with the single crystal neutron diffractometer HEiDi at the FRM-II, Germany. Compared to previous work [3], adding more Rb^+ ions into the crystal structure causes a slight change in the geometry of the oxygen coordination of the Rb^+/Tl^+ site, which is distorted according to the stereochemical activity of the lone-pair electrons of the Tl^+ ions. The fact that the crystal structures of $\text{Rb}_{0.51}\text{Tl}_{0.49}\text{H}_2\text{PO}_4$, $\text{Rb}_{0.46}\text{Tl}_{0.54}\text{H}_2\text{PO}_4$ and TDP are rather similar in the room temperature phase is consistent with the previous NQR investigation results [4] which showed that the mixed crystals $\text{Rb}_x\text{Tl}_{1-x}\text{H}_2\text{PO}_4$ for the composition range $0.2 \leq x \leq 0.8$ are isotopic to TDP. Contrary to TDP, no phase transition was found by NQR for the mixed crystals at low temperature [4]. However, until now, there exists no further investigation concerning a possible phase transition in the Tl^+ -dominated mixed system. Therefore, it could be very interesting to investigate the mixed crystals more systematically and as a function of temperature in order to better understand the role of the lone-pair electrons of the Tl^+ ions for the phase stability and to follow the disorder behavior of the hydrogen atoms.

[1] S. Mattauch, G. Heger, K.H. Michel, *Cryst. Res. Technol.* **2004**, *39*, 1027-1054. [2] I.H. Oh, S. Mattauch, M. Merz, G. Heger, *Acta Cryst. B* **2006**, *62*, 719-728. [3] I.H. Oh, S. Mattauch, G. Heger, C.E. Lee, *Journal of the Physical*

Society of Japan **2008**, *77*, 094602. [4] J. Seliger and V. Zagar, *Physical Review B* **1995**, *52*, 1070-1077.

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Li insertion in ball milled graphitic carbons by total XRD
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Currently a significant research effort is under way worldwide to find advanced negative electrode materials for Li-ion batteries. Graphitic carbon is currently the material of choice because it can accommodate Li atoms fast, reversibly and without generating much mechanical stress. In normal conditions pristine graphitic carbon can accommodate up to one Li atom per six carbon atoms. Real life applications, however, demand higher Li storage capacities and scientists have been looking into ways to go beyond what bulk LiC_6 can offer. It has been found that ball milled graphitic carbons show increased Li storage capacity. The increase has been explained in terms of the "stacks of fallen cards" model which features breaking, upon the impact of ball milling, of the extended graphitic layers into smaller pieces that are randomly oriented with respect to each other thus posing a diminished steric hindrance for Li to intercalate. The increased Li storage capacity, however, has been found to fluctuate with the milling time puzzling scientists for more than a decade. We will present results from total x-ray diffraction [1] and reverse Monte Carlo modeling [2] studies on ball-milled graphitic carbons, both as made and electrochemically lithiated. Experimental and modeling results show that ball milling for short times breaks the graphitic layers into smaller pieces as well as generates extended atomic vacancies. Those increase the overall ability of the material to accommodate lithium. Ball milling for longer times keeps generating even more atomic vacancies in the graphitic layers. Carbon atoms displaced from the layers, however, move in between the layers turning heavily ball milled graphitic carbons into an assembly of almost fused together layers that have an impaired ability to accommodate Li atoms. This helps explain well the initial substantial increase and then decrease in the Li storage capacity of ball-milled graphitic carbons [2]. The study [3] demonstrates the great ability of total x-ray diffraction to provide precise structural information for complex materials that are being increasingly explored for energy applications.

[1] V. Petkov, *Materials Today* **2008**, *11*, 28-38. [2] F. Disma, L. Aymard, L. Dupont, J.M. Tarascon, *J. Electrochem. Soc.* **1996**, *143*, 3959-3972. [3] V. Petkov, A. Timmons, J. Camardese, Y. Ren, *Mat.Chem.* **2011**, in press.

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X-ray and neutron studies of defect formation in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$
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Lithium iron phosphate is a very promising material for applications in Li-ion batteries for electric and hybrid cars [1]. The

electronic and ionic conductivity of the compound can be highly enhanced by nanosizing the particles. Therefore, much effort has been put into developing synthesis pathways for high quality LiFePO₄ nanomaterials[2]. Hydrothermal synthesis is an easy, efficient and environmentally friendly way of producing nanoparticles. However, when synthesized hydrothermally at low temperatures, LiFePO₄ show a high concentration of Li-Fe antisite defects[3].

We have used *in situ* synchrotron SAXS/WAXS and PXRD to study the formation of Li(Fe_{1-x}Mn_x)PO₄ (x=0, 0.25, 0.50 and 0.75) nanoparticles during hydrothermal synthesis. The formation from LiOH, FeSO₄/MnSO₄, and H₃PO₄ involves an unknown intermediate phase, which quickly transforms into Li(Fe_{1-x}Mn_x)PO₄ even at rather low temperatures. The SAXS data show that the intermediate phase consists of small particles that grow, and then transforms into larger particles of Li(Fe_{1-x}Mn_x)PO₄. However, the resulting particles contain a rather large concentration of defects, where Fe occupies a Li site. By means of the time resolved PXRD data, we are able to follow the influence of time, temperature and manganese doping on the defect concentration. It is revealed that even under supercritical conditions a reaction time of several minutes is required to eliminate the defects.

The nature of the defects is studied further by Rietveld refinements of high resolution neutron and X-ray data. The results indicate that the defect is not a true anti-site defect, as no Li is found on the Fe site. Further studies of the defect chemistry of the materials are ongoing, using synchrotron and neutron total scattering data. Here, Pair Distribution Function analysis of both neutron and X-ray diffraction data are used to study the local coordination of the defects.

[1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *Journal of the Electrochemical Society* **1997**, *144*, 1188. [2] J. Tollefson, *Nature* **2008**, *456*, 436. [3] J. J. Chen, M.S. Whittingham, *Electrochemistry Communications* **2006**, *8*, 855.

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Exciting Crystal Chemistry of Mixed Metal-Borohydrides

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The fascinating diversity in the Crystal Chemistry of novel compounds based on the BH₄⁻ group continues to proliferate. In this study we contribute with the structural characterization and classification of the recently found novel ternary borohydrides ASc(BH₄)₄ and K₂M(BH₄)₄ (A=Rb,Cs and M=Mn,Mg), based on bi- and trivalent d-Metals, which are brought into a crystal-chemical context. The present results are in good agreement with the established and ongoing trend of this compound group to form ionic as well as framework structures closely related to oxides, as observed in numerous recent works. It is shown by Synchrotron Powder Diffraction, supported by spectroscopic methods, that structural similarities, e.g. between Mn- and Mg-modifications observed for binary borohydrides [1,2] can be extended to corresponding ternary compounds. The compounds reported here all follow very similar building principles, the most prominent structural unit being the isolated tetrahedral complex anion [M(BH₄)₄]ⁿ⁻ (n = 1, 2) which is charge-compensated by the larger alkaline cation. This results in packed structures, in this case different derivatives of the sulfates. Thus, while evidence for the covalent bonding contribution

in the binary compounds of the respective M metal lies intrinsically in the connectivity of their distinct frameworks, the big complex anion in the ternary ones has various bonding-schemes as a consequence; the interaction between ligands and the central atom of [M(BH₄)₄]ⁿ⁻ being of predominantly covalent character, as deduced by the directionality of hydrogen bonding reported in many works as well as the integrity of the tetrahedron, while on a larger scale the compound crystallizes in well known ionic structure types and their distorted derivatives. The ongoing reports of such structural similarities, culminating in solid solutions, not only extends the promising prospects concerning the precise compositional and structural tunability of this compound class regarding their hydrogen storage properties, but also is a clear hint of structural flexibility with regard to the more complex quaternary structures, which may show greater dependency on structural parameters such as site mixing and occupancies with respect to their physical properties, e.g. Li⁺ conductivity.

[1] Ya. Filinchuk, R. Cerny, H. Hagemann, *Chemistry of Materials* **2009**, *21*, 925-933. [2] R. Cerny, N. Penin, H. Hagemann, Ya. Filinchuk, *Journal of Physical Chemistry C* **2009**, *113*, 9003-9007

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An in-situ synchrotron X-ray powder diffraction study of size dependent phase transitions in nanostructured ZrO₂-Sc₂O₃ solid solutions

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Due to the high ion conductivity exhibited by some of ZrO₂-Sc₂O₃ polymorphs, this material is considered a promising candidate as solid electrolyte for intermediate temperature solid oxide fuel cells. It is well known that the electrical properties of zirconia based solid solutions are strongly dependent on their crystallographic structure, which in turn depends on composition, temperature and thermal history. Polymorphs of several ZrO₂-based systems exhibit monoclinic (m), three forms of tetragonal (t, t' and t'') or cubic (c) symmetries [1]. Only the tetragonal and cubic phases of zirconia based solid solutions usually exhibit electrical properties good enough for practical applications.

In the particular case of ZrO₂-Sc₂O₃, three rhombohedral phases, named as β, γ and δ, are observed at room temperature within a wide range of compositions, but these phases exhibit rather low ion conductivity. In previous works [2,3], we demonstrated that in nanocrystalline powders of ZrO₂-Sc₂O₃ with average crystallite sizes up to 25 nm, a metastable tetragonal t''-form or the cubic phase, depending on the composition, are fully retained at room temperature. These t'' and c phases present high ion conductivity at intermediate temperatures. On the other hand, these materials with an average crystallite size larger than 25 nm exhibit a mixture of c or t'' and β or γ phases.

Many investigations during the last decades focused on the effects of crystallite size over the phase diagrams, but the precise reason why the crystallite size at nanometric scale determines the crystal structure still remains unclear. This issue is relevant also from a technological reason, because it implies that different structures could be tailored by an adequate control of crystallite sizes. Thus the knowledge of the phase diagrams of nanomaterials for different average crystallite sizes is scientifically pertinent and also potentially useful for practical applications.