

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 LiFePO<sub>4</sub> nanomaterials[2]. Hydrothermal synthesis is an easy, efficient and environmentally friendly way of producing nanoparticles. However, when synthesized hydrothermally at low temperatures, LiFePO<sub>4</sub> 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<sub>1-x</sub>Mn<sub>x</sub>)PO<sub>4</sub> (x=0, 0.25, 0.50 and 0.75) nanoparticles during hydrothermal synthesis. The formation from LiOH, FeSO<sub>4</sub>/MnSO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> involves an unknown intermediate phase, which quickly transforms into Li(Fe<sub>1-x</sub>Mn<sub>x</sub>)PO<sub>4</sub> 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<sub>1-x</sub>Mn<sub>x</sub>)PO<sub>4</sub>. 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.

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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 BH<sub>4</sub><sup>-</sup> group continues to proliferate. In this study we contribute with the structural characterization and classification of the recently found novel ternary borohydrides ASc(BH<sub>4</sub>)<sub>4</sub> and K<sub>2</sub>M(BH<sub>4</sub>)<sub>4</sub> (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(BH<sub>4</sub>)<sub>4</sub>]<sup>n-</sup> (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(BH<sub>4</sub>)<sub>4</sub>]<sup>n-</sup> 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<sup>+</sup> conductivity.

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### An in-situ synchrotron X-ray powder diffraction study of size dependent phase transitions in nanostructured ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub> solid solutions

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Due to the high ion conductivity exhibited by some of ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub> 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 ZrO<sub>2</sub>-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 ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub>, 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 ZrO<sub>2</sub>-Sc<sub>2</sub>O<sub>3</sub> 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.