

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.

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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.

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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.

We have determined the phase diagram of nanopowdered ZrO_2 containing 10 to 14 mol% Sc_2O_3 with average crystallite sizes ranging from 30 nm up to 100 nm by X-ray powder diffraction, using the D10B-XPD synchrotron beam line of LNLS (Campinas, Brazil). Our study shows that the boundaries of c or t'' , β and γ phases strongly depend on both, Sc_2O_3 content and crystallite size. The transition temperatures related to cooling and heating processes decrease for decreasing crystallite sizes. In addition, the experimental results corresponding to a whole heating/cooling cycle indicate the presence of a clear hysteresis effect.

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Synchrotron XRD and XAS studies of nanocrystalline ZrO_2 - Y_2O_3 solid solutions

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Because of their excellent mechanical and electrical properties, zirconia-yttria (ZrO_2 - Y_2O_3) solid solutions are being widely investigated, in particular because it is a potential candidate to be used as electrolyte in solid state oxide fuel cells. An important analysis of these material properties is related to their dependence on nanoscopic scale and composition.

The crystallographic structure and short range order of a series of nanocrystalline ZrO_2 - Y_2O_3 solid solutions with varying Y_2O_3 content was studied by synchrotron radiation X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Powdered samples were synthesized by a pH-controlled nitrate-glycine gel-combustion process. Our XRD results indicate the presence of the t' -form of the tetragonal phase ($c/a > 1$) in samples with up to 8 mol% Y_2O_3 , and the t'' -form ($c/a = 1$) for 10 mol% Y_2O_3 . Notice that in the t'' -form the oxygen anions are displaced from their ideal positions in the fluorite type structure of the cubic phase. For solid solutions with Y_2O_3 contents higher than 11 mol% the cubic phase is observed. The t'/t'' and t'' /cubic compositional boundaries were determined to be at (9 ± 1) and (10.5 ± 0.5) mol% Y_2O_3 , respectively. These composition limits agree well with those reported by Yashima et al [1] for materials composed of larger (micrometric) crystallites synthesized by arc melting followed by a rapid quenching. The c/a ratios of the t' -form determined for the nanostructured polycrystals studied here are slightly smaller than those determined by Yashima et al.[1] for powders composed of larger (micrometric) crystallites.

A complementary XAS study of the same ZrO_2 - Y_2O_3 solid solutions near the absorption edges of Zr and Y demonstrated that the t'' /cubic transition is related to a tetragonal-to-cubic symmetry change of the first oxygen coordination shell around Zr atoms, without any significant changes in the environment of Y atoms.

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Large anharmonicity in end members of $AgPb_mSbTe_{2+m}$

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Thermoelectric materials are functional materials with the ability to interconvert electrical and thermal energy, which make them applicable in active cooling and power generation through exploitation of waste heat. The thermoelectric figure of merit, zT , is optimized in materials with low thermal conductivity, low electric resistivity and high thermopower. The solid solution of $AgPb_mSbTe_{2+m}$, also known as LAST (Lead-Antimony-Silver-Tellurium), has in recent years been intensively investigated due to their promising thermoelectric properties. Several of the available commercial thermoelectric modules are based on the LAST compounds. The materials are power generators used in space crafts, military applications and pacemakers. The end member compounds $AgSbTe_2$ ($m = 0$) and $PbTe$ ($m = \infty$) have been reported to have extremely low lattice thermal conductivities of 0.63 and 2.4 W/mK, respectively.[1] The value for $AgSbTe_2$ is close to the minimum possible value. To understand and explain these physical properties of the advanced crystallographic studies have been performed.

Both $AgSbTe_2$ and $PbTe$ are semiconducting ionic compounds crystallizing with the rocksalt structure in the cubic space group $Fm-3m$. Multi-temperature synchrotron powder diffraction data between 90 and 1000 K have been measured at Spring8 at a wavelength of $\lambda = 0.50007 \text{ \AA}$ and subsequently Rietveld refined. The refined unit cell axes show near linear thermal expansion and the refined atomic displacement parameters have been modeled using the Debye model. Furthermore, the Rietveld refinements indicate structural disorder in the rocksalt structure. The disorder partly explains the low thermal conductivities.

An additional effect lowering the thermal conductivities is large anharmonicity of the chemical bonds in the crystals, revealed by high Grüneisen parameters of 2.0 and 1.5 for $AgSbTe_2$ and $PbTe$, respectively.[1] It is believed that anharmonicity of the chemical bonds drives the phonon-phonon umklapp and normal processes that intrinsically limits the high temperature lattice thermal conductivity.[2] The anharmonicity have been investigated through high and low temperature high-resolution neutron single crystal diffraction data obtained at the Lujan Center, Los Alamos National Laboratory. From these data the nuclear density and anharmonicity are refined using Gram-Charlier coefficients and from the low and high temperature refinements the positional disorder and the anharmonicity of the atoms can be separated.

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