Posters

**MS39.P15**


**An in-situ synchrotron X-ray powder diffraction study of size dependent phase transitions in nanostructured ZrO$_2$-Sc$_2$O$_3$ solid solutions**

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Due to the high ion conductivity exhibited by some of ZrO$_2$-Sc$_2$O$_3$ 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$_2$-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$_2$-Sc$_2$O$_3$, 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$_2$-Sc$_2$O$_3$ 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.

Keywords: borohydride, powder diffraction, hydrogen storage

**MS39.P14**


**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$_4$ group continues to proliferate. In this study we contribute with the structural characterization and classification of the recently found novel ternary borohydrides $\text{ASe(BH}_4)_n$ and $\text{K}_m\text{M(BH}_4)_n$ ($\text{A}=$Rb, Cs and $\text{M}=$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 $\text{[M(BH}_4]_n}^\text{2+}$ ($\text{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 $\text{[M(BH}_4]_n}^\text{2+}$ 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. $\text{Li}^+$ conductivity.

**Keywords:** battery materials, defects, in situ


**MS93.P1**


**Keywords:** battery materials, defects, in situ