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Phase Transitions of Alluminosilicate Refractories by Temperature Resolved XRD

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Aluminium-ceramic composites which grow in melting and holding furnaces at the interface between liquid aluminum and alluminosilicate refractories are of great technological impact. These materials cause serious problems to aluminum alloys production management, since they damage the refractory material and in turn the furnace.

However, in the literature very few papers have faced a systematic study of chemical composition, structure and microstructure of aluminium-ceramic composites [1], [2]. This is a compulsory step to understand the physico-chemical phenomena which generate the composites and then to asses innovative procedures to avoid them.

We began to investigate formation of aluminum-ceramic composites by temperature resolved X-ray diffraction (XRD). The XRD probe was exploited for tracking the composite structure during its formation upon heating in a proper furnace for high-temperature experiments based on a previous model [3] and adapted on an horizontal Bragg-Brentano goniometer. In our contribution the preliminary results of the study will be presented and discussed.

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Keywords: refractories, high-temperature diffractometry, phase transitions and structure

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Characterization of Shape-Preserving Diatom Displacement Reactions using High Temperature X-ray Diffraction

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Shape preserving displacement reactions of the type 2Mg(s) + SiO_2(s) > 2MgO(s) + {Si} and TiF_4(g) + SiO_2(s) > TiO_2(s) + SiF_4(g) where the SiO_2 is in the form of diatoms were studied using high temperature x-ray diffraction (HTXRD) with the samples sealed inside graphite reaction vessels. Enclosure of the sample within the graphite cell allows for containment of the vapor formed during the reaction (Mg(g) and TiF_4(g) respectively). Reactions of this type allow for complete conversion of the complex-shaped SiO_2 diatom frustule to alternate chemistries (such as MgO and TiO_2) with no loss of structural features. HTXRD measurements show complete conversion of SiO_2 to MgO after approximately one hour at 700°C, and after 45 minutes for SiO_2 to TiO_2 at 300°C. The kinetics of both reactions were also probed using isothermal measurements.

Keywords: diatoms, shape preserving, displacement reactions

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Low-temperature Phase Transitions for Solid Solutions of TbVO4/DyVO4

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Structural phase transitions of the isostructural vanadates TbVO4 at about 32 K and DyVO4 at about 14 K have been known for quite some time and are frequently used as reference temperatures in low-temperature diffraction experiments. Although both low-temperature phases are orthorhombic, the respective structures are decisively different as clearly indicated by the splitting of different reflections in the powder patterns when cooling the tetragonal high-temperature forms. We have studied solid solutions of these two vanadates to investigate the potential interplay of two structural transitions.

Keywords: phase transitions in solids, powder diffraction, rare-earth compounds

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Magneto-structural Phenomena in Hydrides with Unusual Topology of Spin Lattice

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Recently, we found highly unusual coupling between the magnetic and chemical (hydrogen) orderings in the hexagonal Laves hydrides RMn_2H_x (R=Er, Tm and Lu; 2<x<4.6). RMn_2 compounds have very unusual topology of the Mn-sublattice resulting in a fully degenerated magnetic ground state. Tiny modifications of the H-superstructure can stabilize or destroy different types of magnetic orderings. The magneto-structural coupling results in oscillating dependence between the magnetic and structural ordering parameters. While the H-sublattice becomes gradually more ordered as the H density increases, the correlation length in the magnetic sublattice shows an oscillating dependence with H content [1]. The key role of the H-superstructure in formation of magnetic ordering manifests by strong sensitivity of magnetic and structural properties to applied pressure. In $RMn_2H_{4.6}$ small applied pressure (0.6GPa) sets the new arrangement of the H atoms. Changes in local environment of the magnetic atoms result in the suppression of the long-range magnetic order in the high-pressure phase [2]. Another intriguing phenomena were found near the frontier between localized and intrinsic magnetic states of Mn-sublattice in the low-content hydrides $(Er_xLu_{1-x})Mn_2H_3$ (0<x<1). We observed giant magnetovolume effect ($\delta V/V$=2.5%) and unusual phase decoupling, involving antiferromagnetic domains with different wave vectors.

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Keywords: magnetic frustration, hydrides, neutron diffraction

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Low Temperature Structures of the Metal Oxyhalides *MOX*: *M* = Ti, V and *X* = Cl, Br

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The metal(III) oxyhalides *MOX* structures with *M* = Ti, V and *X* = Cl, Br [1] are isostructural with FeOCl at room temperature: they are built by slabs consisting of a M_2O_2 bilayers enclosed by layers of *X* atoms. The symmetry is orthorhombic, space group *Pmmn*. In TiOCl and TiOBr two structural phase transitions have been observed in the magnetic properties upon cooling, suggesting the presence of a spin-Peierls state [2,3]. The low temperature phase is a twofold superstructure of the room temperature phase [4]. In VOCl only one phase transition is observed [5].

We have performed temperature dependent single crystal X-ray diffraction experiments down to T = 10 K, exploring the development of various superstructures in the low temperature and intermediate temperature phases of these compounds. The knowledge of the superstructures is important, because it might shed further light on the nature of the phase transitions in the *MOX* compounds.

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