

P.20.09.2*Acta Cryst.* (2005). A61, C470**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 assess 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.

[1] Afshar S., Allaire C., Jom-J., *Min. Met. Mat. S.*, 2000, **52** (5), 43-46. [2] Wynn A.M., *Brit. Ceram. Trans. J.*, 1992, **91** (5), 153-158. [3] Filippini A., Borowski M., Bowron D.T., Ansell S., De Panfilis S., Di Cicco A., Itié J.P., *Rev. Sci. Instr.*, 2000, **71**, 2422-2432.

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

P.20.09.3*Acta Cryst.* (2005). A61, C470**Characterization of Shape-Preserving Diatom Displacement Reactions using High Temperature X-ray Diffraction**

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Shape preserving displacement reactions of the type $2\text{Mg(s)} + \text{SiO}_2\text{(s)} > 2\text{MgO(s)} + \{\text{Si}\}$ and $\text{TiF}_4\text{(g)} + \text{SiO}_2\text{(s)} > \text{TiO}_2\text{(s)} + \text{SiF}_4\text{(g)}$ 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 $\text{TiF}_4\text{(g)}$ 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

P.20.09.4*Acta Cryst.* (2005). A61, C470**Low-temperature Phase Transitions for Solid Solutions of TbVO4/DyVO4**

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Structural phase transitions of the isostructural vanadates TbVO_4 at about 32 K and DyVO_4 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

P.20.10.1*Acta Cryst.* (2005). A61, C470**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 ($\text{R}=\text{Er}$, 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 $\text{RMn}_2\text{H}_{4.6}$ 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 $(\text{Er}_x\text{Lu}_{1-x})\text{Mn}_2\text{H}_3$ ($0 < x < 1$). We observed giant magnetovolume effect ($\delta V/V=2.5\%$) and unusual phase decoupling, involving antiferromagnetic domains with different wave vectors.

[1] Makarova O.L., Goncharenko I. N., Bouree F., *Phys. Rev. B*, 2003, **67**, 134418. [2] Makarova O.L., Goncharenko I.N., Le Bihan T., *Solid State Com.*, 2004, **132**, 329.

Keywords: magnetic frustration, hydrides, neutron diffraction

P.20.10.2*Acta Cryst.* (2005). A61, C470-471**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 $M = \text{Ti}$, V and $X = \text{Cl}$, 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.

[1] Schäfer H., Wartenpfehl F., Weise E., *Z. Anorg. Allg. Chemie*, 1958, **295**, 268. [2] Seidel A., Marianetti C.A., Chou F.C., Ceder G., Lee, P.A., *Phys. Rev. B*, 2003, **67**, 020405. [3] Sasaki T., Mizumaki M., Kato K., Watabe Y., Nishihata Y., Takata M., Akimitsu J., *arXiv:cond-mat*, 2005, 0501691. [4] Shaz M., van Smaalen S., Palatinus L., Hoinkis M., Klemm M., Horn, S., Claessen, R., *Phys. Rev. B*, 2005, *in press*. [5] Wiedenmann A., Venien J.P.,

Palvadeau P., Rossat-Mignod J., *J. Phys. C: Solid State Phys.*, 1983, **16**, 5339.

Keywords: phase transitions, superstructure, TiOCl TiOBr VOCl

P.20.10.3

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Studies of the Magnetic Ordering in Polycrystalline Cr-Ru Alloys by Neutron Powder Diffraction

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The magnetic phase diagram of the Cr-Ru alloy system [1,2] shows that the spin density wave (SDW) ordering below the Néel temperature is incommensurate (I) for Ru concentrations (x) < 1%, commensurate (C) for $1\% < x < 17\%$, with the formation of a superconducting state for $x > 17\%$ [2].

Our approach to identify the nature of the magnetic ordering has always encompassed neutron diffraction studies on single crystal samples in which the different SDW orderings give rise to specific intensity distributions around the {100} reciprocal lattice position [3].

We here report experimental results from neutron powder diffraction studies of polycrystalline samples with $x = 0.3\%$, 12.5% and 15% representative of the I and C phases. This has become an option with the availability of the upgraded neutron powder diffraction instrument at the SAFARI-1 research reactor.

The results demonstrate the viability of using diffraction pattern distributions from polycrystalline samples to research intricacies in the magnetic ordering of dilute alloys of Cr in future studies.

[1] Fawcett E., Alberts H.L., Galkin V. Yu., Yakhmi J.V., *Rev. Mod. Phys.*, 1994, **66**, 25. [2] Chatani K., Endoh Y., *J. Phys. Soc. Japan*. 2003 **72**, 17. [3] Boshoff A.H., Alberts H.L., du Plessis P. de V., Venter A.M., *J. Phys. Condens. Matter*, 2003 **5** 5353.

Keywords: neutron powder diffraction, spin-density wave, magnetic phases

P.20.10.4

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Magnetic Transitions in $\text{ErCo}_{10}\text{Mo}_{2-x}\text{M}_x$ ($\text{M}=\text{Si}$ and V)

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The intermetallic compounds of the type $\text{R}(\text{T},\text{M})_{12}$ ($\text{R}=\text{rare earths}$, $\text{T}=\text{Fe, Co, Ni}$ and $\text{M}=\text{stabilizing elements like Mo, Si, V}$ etc) that find many applications as permanent magnet materials exhibit tunable magnetic characteristics. Tuning of the magnetic anisotropy values, Curie and spin reorientation temperatures are made possible by replacing the constituting elements with others in specific proportions. X-ray powder diffraction and low field magnetization studies on $\text{ErCo}_{10}\text{Mo}_{2-x}\text{M}_x$ ($\text{M}=\text{Si, V}$) in the temperature range between 5K - 800K have revealed that:

i) all members of the family crystallize in ThMn_{12} type structure with tetragonal I4/mmm space group.

ii) Si for Mo replacement leads to a linear decrease of lattice parameters, a significant shift of T_c from 425K to 719K and a T_{sr} reduction from 139K to 74K.[1]

iii) V for Mo replacement leads to a linear decrease of lattice parameters, no significant change in T_c and a strong shift of primary T_{sr} from 139 to 350K.[2]

These findings together with structural and magnetic transition implications will be presented.

[1]Zhao Z.G., de Groot C.H., Brück E., Buschow K.H.J., de Boer F.R., *Physica B*, 1996, **228**, 214. [2] Brabers J.H.V.J., Zhou G.F., de Boer F.R., Buschow K.H.J., *J. Mag. Mag. Mat.*, 1993, **118**, 339-346.

Keywords: spin reorientation, Curie temperature, magnetic anisotropy

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X-ray Diffraction and Absorption Study under Strong Pulsed Magnetic Fields

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Diffraction experiments under non-ambient conditions have been developed for decades. Nowadays x-ray experiments over 100 GPa can be carried out using a diamond anvil cell. For ultra-low-temperature experiments, neutron and x-ray experiments below a few hundred mK are performed at several places. In contrast, diffraction experiments under strong magnetic field are limited below about 20T.

Recently, we have developed very small pulsed magnets [1]. Typical dimensions of the coils are 20 mm in diameter and 25 mm in length. Hence, the coil is readily attached to the cold head of a conventional closed cycle refrigerator, and is easily installed in a conventional x-ray diffractometer. Although the coils are small, magnetic fields above 30 T can be generated. Using this miniature coil and intense synchrotron x-rays, we conducted x-ray diffraction experiments under strong pulsed magnetic fields at beamline BL22XU at SPring-8. The field induced structural phase transition around 9 T in $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and the valence transition around 26 T in YbInCu_4 were clearly observed. Our new plan for x-ray absorption experiments under pulsed magnetic fields is also presented.

[1] Matsuda Y.H., et al., *Physica B*, 2004, **346-347**, 519.

Keywords: pulsed magnetic field, magnetic structural phase transition, valence fluctuations

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Magnetic field induced polymorphism of R_5T_4 compounds

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Structural rearrangements triggered by a magnetic field are rare compared to temperature and/or pressure induced polymorphism. While the latter is routinely probed *in situ* by temperature and pressure dependent powder diffraction, the most common tools employed in detecting magnetic field induced polymorphism remain bulk field-dependent measurements of the physical properties, e.g., the electrical resistance, magnetization and strain. On one hand, discontinuities in these macroscopic properties serve as suitable evidence of a structural phase transition, but on the other hand, they provide no clues about its atomic-scale mechanism. By successfully coupling a rotating anode powder diffractometer with a continuous-flow cryostat and a split-coil superconducting magnet we were able to obtain excellent-quality Rietveld-ready powder diffraction data between 2.5 K and 315 K in 0 to 4 T magnetic fields. This allowed us to study the magnetic field-induced polymorphism in several polycrystalline compounds from the R_5T_4 family, where $\text{R} = \text{lanthanide metal}$, $\text{T} = \text{Si, Ge and/or Sn}$.

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Keywords: phase transitions, powder diffractometry, structural physical properties

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When 2+2 isn't 4

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Recently much work has gone into examining the photoexcited HS state of iron(II) spin crossover compounds in full structural detail[1]. So far this work has focused on compounds closely related to the early work with either two neutral tridentate ligands or two