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In the work structure mechanisms of Mn segregation from solid solutions with perovskite-like and spinel structure were investigated. The complex Mn-content oxides are often used as catalysts. Spinel ($Mn_{3-x}Al_xO_4$) are known as catalysts of deep oxidation. The $La_{1-x}Ca_xMnO_3$ solid solutions with the perovskite-like structure are catalysts for the partial oxidation of methane. In both systems an active component of catalysts is manganese oxide which is formed under catalytic reaction conditions. Spinel catalysts are activated by heating under oxidizing atmosphere. Perovskite catalysts are used under reducing atmosphere. To simulate real conditions of catalytic processes we applied high-temperature XRD in the air (oxidizing atmosphere) and in the vacuum (reducing atmosphere). Mn-content spinel ($Mn_{1.5}Al_{1.5}O_4$) is stable under heating in the vacuum: spinel keeps structure and composition. On the contrary decomposition is observed in the air during heating in the air. Nanocrystalline phases of β - Mn_3O_4 and spinel $Mn_{2.4}Al_{0.4}O_4$ are the products of decomposition. The lattice parameter of cubic phase decreases from 8.285 Å to 8.043 Å when sample was heated from ambient temperature to 700°C. This fact shows change of spinel composition from $Mn_{1.5}Al_{1.5}O_4$ to $Mn_{0.4}Al_{2.4}O_4$, i.e. manganese ions leave the structure. TEM data indicates that small particles of β - Mn_3O_4 are appeared on the surface of the well crystallized cubic spinel when sample was calcined at the temperature of 300-400°C. After further increase calcination temperature β - Mn_3O_4 particles grow. As a result we can conclude that Mn cations segregation from initial spinel occurs with formation of new phase β - Mn_3O_4 . At the same time spinel $Mn_{1.5}Al_{1.5}O_4$ transforms to aluminum-enriched spinel $Mn_{0.4}Al_{2.4}O_4$ with statistical distribution of cation vacancies. Temperature stability of the series of samples $La_{1-x}Ca_xMnO_3$ ($0 \leq x \leq 1$) was investigated using in situ XRD (vacuum and air atmosphere). According to TEM and XRD analysis the microstructure and phase structure of samples keeps during heating in the air. To model a process of catalysis reduction in the reactor we heated samples in the vacuum. According to TEM data multiple planar defects in perovskite structure were formed starting from $x=0.3$, the amount of the defects grows with the increase of x value. In the sample with the $x=0.9$ areas of the planar defects segregation and superstructure formation is observed. According to EDX analysis in these areas the deficit of Mn cations (~20%) is detected. The superstructure is characterized by quadruple period of the crystal lattice in [001] direction. Thus Mn cations segregation was observed in the both systems. In the spinel oxide segregation is accompanied by partial oxidation of Mn^{2+} to Mn^{3+} due to oxygen embedding. In the perovskite oxides part of Mn cations transform to Mn^{3+} due to oxygen loss in the vacuum conditions. Microstructure of systems changes by different ways during high-temperature treatment. Planar defects are formed in the perovskite oxides, statistical distribution of cation vacancies is observed in spinel oxide. This work was supported by the integration project SB RAS №36 and the grant under the program "Development of scientific potential of the higher school" №2.1.1/729.

Keywords: catalyst structure, manganese compounds, in situ diffraction

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High-pressure structure and compressibility of ZnAl-CO₃ LDHs. Jolanta Darul^a, Waldemar Nowicki^a, Paweł Piszora^a, Christian Lathe^{b,c}, ^aFaculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, PL-60780 Poznań, Poland. ^bHASYLAB at DESY, Notkestrasse 85, D-22603 Hamburg, Germany. ^cGFZ German Research Centre for Geosciences, Dept. 5, Telegraphenberg, Potsdam, D-14473, Germany. E-mail: jola@amu.edu.pl

Layered double hydroxides (LDHs) are a class of ionic lamellar compounds that consist of positively charged host layers with two kinds of metallic cations and exchangeable hydrated anions located in the interlayer gallery for charge balance. The charge of the layers arises from the substitution of a part of the divalent metal ions with trivalent ones. Metal ions are octahedrally coordinated by six oxygen atoms belonging to six OH groups. Each OH group is shared by three octahedral cations [1]. The structural compression mechanism of ZnAl-CO₃ LDHs was investigated by energy dispersive synchrotron powder X-ray diffraction up to 6,5 GPa using a multianvil press (beamline F2.1., HASYLAB/DESY, Hamburg). Our samples have the polytype 3R₁ (the layer stacking sequence: AC CB BA AC..., space group $R\bar{3}m$), according to simulated XRD patterns. The expected [2] high-pressure-induced amorphization was not observed, even in the case of samples compacted at 6,5 GPa. The X-ray patterns of bulk samples showed a decrease in the intensity for all peaks, being more expressive for the basal d-spacing. However, the peak intensity was recovered after grinding these samples. Although both cell parameters a and c decrease with increasing pressure, the rate of contraction in c is much larger than that in a (the thickness of the octahedral layer only shows a slight decrease, whereas the interlayer spacing contracts rapidly). In other words, the c -axis is about 3 times more compressible than a . Since the electrostatic forces between neighboring sheets (in the interlayer) are much weaker than those within the sheets themselves, the structure is more flexible along the c axis than in the (001) plane.

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Neutron diffraction on functional materials at extreme conditions. Markus Hoelzel^a, Francesco Dolci^b, Eveline Weidner^b, Jianjiang Hu^c, Wolfgang Schmahl^d, Casjen Merkel^d, Manuel Hinterstein^a, Norbert Juenke^e, Hartmut Fuess^a, ^aMaterials Science, Technical University Darmstadt, Germany. ^bInstitute for Energy, Joint Research Centre, Petten, Netherlands. ^cInstitute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany. ^dDepartment of Earth- and Environmental Sciences, Ludwig-Maximilians

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In this contribution recent results by neutron diffraction on technological important functional materials are reported. Hydrogen storage materials, shape memory alloys and ferroelectrics were investigated under special environmental conditions: hydrogen pressure, mechanical load or electrical fields, respectively. All experiments were carried out at the high-resolution neutron powder diffractometer SPODI (FRM-II, Garching). This instrument offers possibilities for the in-situ analysis of functional materials under special environmental conditions.

A rotatable load frame available at SPODI allows materials characterisation at different orientations of the load axis with respect to the scattering vector. Besides tensile stress, also pressure and torsion can be applied. Monoclinic nickel titanium shape memory alloys were measured at different strain levels to determine load-induced elastic strains, changes in twinning texture and resulting microstrains. In addition, diffraction studies under different sample orientations (i.e. different orientations of load axis) were carried out to analyse the anisotropy of the elastic response.

Hydrogen storage materials of the system LiD/Mg(ND)₂ were investigated at 220 °C and different deuterium pressures (up to 70 bars) to study the phase transformation behaviour during desorption and re-deuteration. It has been shown that the deuteration occurs via intermediate reaction steps. The appearing phases could be structurally analysed by Rietveld refinement.

An apparatus for high electric fields was developed to analyse the poling mechanisms in ferroelectrics at fields up to 7 kV/mm. The studies were carried out on samples of technological relevant systems like PbZr_xTi_{1-x}O₃ with compositions close to the morphotropic phase boundary as well as lead-free ferroelectrics of system NBT-BT-KNN. Here, the electrical field induced strain could be correlated with a field-induced phase transformation. The phase transition is accompanied by a change of the oxygen octahedral tilt system correlated with superlattice reflections in the neutron diffraction patterns.

Keywords: hydrogen storage, ferroelectrics, shape memory alloys

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Effect of high pressure treatments on the structure of R₂(MoO₄)₃ (R=Eu, Gd, Sm) single crystals. Elena Kudrenko, Salavat Khasanov, Semen Shmurak, Boris Redkin, Vitaly Sinitsyn. *Institute of Solid State Physics RAS, Chernogolovka, Russia.*

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Early was established [1] that powder samples of some rare earth molybdates undergo phase transformation from initial metastable crystalline β'-phase to the amorphous state at relatively moderate pressures ~7-9 GPa. However treatments of Eu₂(MoO₄)₃ single crystal samples in the same pressure range displayed more complex X-ray pattern [2]. To clarify the structural peculiarities of the transformation the number of R₂(MoO₄)₃ (where R = Eu, Gd, Sm) single crystal samples

were investigated by X-ray method after their high pressure treatment at P=9 GPa.

It was found that X-ray diffraction patterns of the "treated" single-crystal samples can be represented as diffuse-like scattering rings and strong sharp peaks within the first diffuse ring ($\leq 0.3 \text{ \AA}^{-1}$). The observed diffraction peaks were indexed in the framework of the orthorhombic lattice with a parameters $a = 9.69 \text{ \AA}$, $b = 10.61 \text{ \AA}$, $c = 19.25 \text{ \AA}$ and $V = 1977 \text{ \AA}^3$ (for R = Eu) which corresponds to the decrease of the cell volume on ~15% in compare with initial β'-phase ($V=1166 \text{ \AA}^3$). Integration and reduction of the diffraction patterns to Debye patterns show that the diffuse scattering is considerably higher than the Bragg diffraction. This means that the most part of the crystal sample is composed of amorphous-like structure and contain crystalline inclusions. These nanocrystalline domains are highly correlated over the sample, due to what high pressure phase produces single-crystal diffraction patterns. Luminescence spectra measured at different wavelengths revealed that such unusual structural state is the characteristic of whole sample. It was found that "treated" single-crystal samples returned to the initial β'-structure at heating to 550°C.

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XIPHOS: Expanding the experimental envelope to extreme sample environments. M.R. Probert, J.A.

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The details of a newly installed and configured high intensity single crystal X-ray diffractometer, XIPHOS, will be presented. This machine has been designed for structural investigations under combined extremes of sample environments, i.e. high pressure, very low temperature and light irradiation. XIPHOS provides a unique facility giving unparalleled access to 'in house' diffraction data, as for example a minimum temperature of 1.9 K. The major components of the system and their complementary aspects will be outlined, highlighting the potential experimental conditions that can be achieved. Methodologies for the operation and monitoring of the system will also be demonstrated together with examples of its research capabilities. Additionally, the development of a new dispex vacuum chamber, to allow irradiation of samples by a laser beam without thermal contact to the outer vacuum sleeves, will be discussed. Irradiation of crystalline samples at reduced temperatures allows the study of different electronic states under the same thermal conditions. Finally, we will highlight some of the unlocked potential in manufacturers programs and also the need for novel solutions to allow operation under extreme environmental conditions.