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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  $\beta$ - $Mn_3O_4$  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  $\beta$ - $Mn_3O_4$  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  $\beta$ - $Mn_3O_4$  particles grow. As a result we can conclude that Mn cations segregation from initial spinel occurs with formation of new phase  $\beta$ - $Mn_3O_4$ . 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

## FA2-MS19-P09

**High-pressure structure and compressibility of ZnAl-CO<sub>3</sub> LDHs.** Jolanta Darul<sup>a</sup>, Waldemar Nowicki<sup>a</sup>, Paweł Piszora<sup>a</sup>, Christian Lathe<sup>b,c</sup>, <sup>a</sup>Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, PL-60780 Poznań, Poland. <sup>b</sup>HASYLAB at DESY, Notkestrasse 85, D-22603 Hamburg, Germany. <sup>c</sup>GFZ German Research Centre for Geosciences, Dept. 5, Telegraphenberg, Potsdam, D-14473, Germany. E-mail: [jola@amu.edu.pl](mailto: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-CO<sub>3</sub> 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 3R<sub>1</sub> (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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## FA2-MS19-P10

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