

ordering reactions called premartensitic transitions, bcc \rightarrow B2 and bcc \rightarrow DO₃, on cooling from high temperatures. On further cooling, martensitic transformation occurs by two or more lattice invariant shears on a {110}-type plane of austenite matrix called basal plane for martensite together with Bain distortion. Bain distortion consists of an expansion of 26% parallel to the [001] _{β} axis and a compression of 11% normal to this axis, and a delineated fct unit cell in the long range order β -phase undergoes to the corresponding fcc lattice with this distortion.

Martensite phase has the unusual layered structures called as 3R, 9R or 18R martensites with low symmetry depending on the stacking sequences on the close-packed planes of the matrix.

The basal plane of martensite is subjected to the hexagonal distortion with martensite formation on which atom sizes have important effect. In case the atoms occupying the lattice sites have the same size, the basal plane of martensite becomes regular hexagon. Otherwise the deviations occur from the hexagon arrangement of the atoms in case atom sizes are different. martensite.

In the present contribution, x-ray diffraction and transmission electron microscopy (TEM) studies were carried out on two copper based ternary alloys, CuZnAl and CuAlMn.

Key Words: Shape memory effect, martensitic transformation, layered structures.

FA2-MS19-P06

Pressure-induced phase transition of KIO₃.

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KIO₃ is a promising material for optical applications as it is transparent in a large frequency range and shows significant non-linear optical effects [1-2]. KIO₃ crystallizes in space group *P1* [3]. The iodine atom environments consist of three oxygen atoms, defining a pyramidal IO₃ group, and three more distant oxygen atoms completing a distorted octahedron. There have been several studies of temperature-induced structural phase transitions in KIO₃ [4-6], but the response to pressure has not been investigated yet.

In this work we present the results of our investigation of the pressure induced phase transition of KIO₃ using X-ray diffraction, Raman spectroscopy, second harmonic generation (SHG) measurements and DFT-based calculations.

Powder X-ray diffraction has been performed on KIO₃ up to 20.9 GPa at the Advanced Light Source, ALS (Berkeley), on beam line 12.2.2 using 25 keV radiation. Raman spectra were collected with an in-house Renishaw micro-spectrometer. The pressure dependence of the SHG signals was measured with Nd:YLF laser ($\lambda = 1054$ nm).

The triclinic crystal structure of KIO₃ is stable up to 7 GPa where a phase transition is detected. The pressure at which the phase transition takes place obtained by X-ray diffraction agrees well with the pressure obtained by the Raman measurements. The lattice parameters and probable space group *P3* of the high-pressure phase were obtained from powder crystal data in situ at 10 GPa. The lattice parameters are $a = 5.998(2)$ Å, $c = 13.896(2)$ Å, $Z = 6$ at 10 GPa. Atomic positions were then obtained using density functional theory.

A second phase transition is detected around 14 GPa. This transformation is followed by a continuous degree of amorphization upon increasing pressure. The ambient-pressure crystal structure is recovered once the pressure is released. The crystal structure determination of the first high-pressure phase and its structural compression mechanism will be discussed.

Financial supports from the DFG (project SPP1236) and COMPRES are gratefully acknowledged. We are grateful to the ALS for beam time. We thank A. Woodland for access to the micro-Raman spectrometer.

[1] Bergman, J.G.; Boyd, G.D.; Ashikin, A.; Kurtz, S.K., *J. Appl. Phys.* 1969, 40, 2860. [2] Landolt-Börnstein, Vol. III/30b, Springer, 2000, 62. [3] Lucas, B.W., *Acta Cryst.* 1984, C40, 1989. [4] Herlach, F., *Helv. Phys. Acta.* 1961, 34, 305. [5] Maeda, M.; Takagi, M.; Suzuki, I., *J. Phys. Soc. Jpn.* 2000, 69, 267. [6] Kasatani, H.; Aoyagi, S.; Kuroiwa, Y.; Yagi, K.; Katayama, R.; Terauchi, H., *Nucl. Instrum. Meth. B.* 2003, 199, 49.

Keywords: high-pressure phase transformations, nonlinear optical materials

FA2-MS19-P07

New Layered High-Pressure Phase of AsS. N.B.

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For arsenic sulfides, one layered covalent compound As₂S₃ and several molecular phases such as As₄S₄, As₄S₃ and others have been known so far. Under high pressures > 4 GPa and temperatures > 670 K the molecular phase As₄S₄ transforms into a new covalent modification with a layered orthorhombic structure (sp. gr. *Pbc2₁*; unit-cell values are $a = 7.4537(7)$, $b = 10.270(2)$, $c = 18.258(1)$ Å). This high-pressure modification of AsS is metastable at normal pressure up to 530 K and represents a chemically stable narrow-gap (~0.8 eV) semiconductor. New structure is noticeable for the presence of covalent bonds between the same type of atoms (As-As) and anomalous weak covalent bonds between dissimilar atoms (As-S) with lengths (2.35 – 2.5 Å) “atypical” of this bond; some structure disordering has also been observed. Obviously, many of the known pseudo-molecular compounds such as As₄S₃, As₄Se₄, P₄S₃, P₄Se₄ and others should transform under high pressure to new covalent layered-structure modifications as well.

The work was done with the partial support of the grant RFBR 10-05-00092 and the grant of leading scientific schools NSh-4034.2010.5.

Keywords: high-pressure phases, structure analysis, layered compounds

FA2-MS19-P08

Structure mechanism of decomposition of Mn₃.

_xAl_xO₄ and La_{1-x}Ca_xMnO₃ solid solutions. Olga Bulavchenko^{a,b}, Evgeny Gerasimov^{a,b}, Svetlana Cherepanova^{a,b}, Sergey Tsybulya^{a,b}, Lubov Isupova^a. ^a*Boreskov Institute of Catalysis SB RAS, Russia.*

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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

FA2-MS19-P09

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.

This research is partially supported by the Ministry of Science and Higher Education (Poland), grant No. NN204330537. The diffraction experiment leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 226716.

[1] Thomas G.S., Radha A.V., Kamath P.V., Kannan S., *J. Phys. Chem. B*, 2006, 110, 12365. [2] Rodrigues J.C, Costa T.M.H, Gallas M.R, Moro C.C., *Phys. Chem. Minerals*, 2009, 36, 439.

Keywords: high-pressure, energy-dispersive X-ray diffraction, layered materials

FA2-MS19-P10

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