

Universität München, Munich, Germany. <sup>e</sup>Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Göttingen, Germany.  
E-mail: [markus.hoelzel@frm2.tum.de](mailto:markus.hoelzel@frm2.tum.de)

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)<sub>2</sub> 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<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> 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**

#### FA2-MS19-P11

**Effect of high pressure treatments on the structure of R<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (R=Eu, Gd, Sm) single crystals.** Elena Kudrenko, Salavat Khasanov, Semen Shmurak, Boris Redkin, Vitaly Sinitsyn. *Institute of Solid State Physics RAS, Chernogolovka, Russia.*

E-mail: [lenak@issp.ac.ru](mailto:lenak@issp.ac.ru)

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 Eu<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> 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 R<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (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.

The work was supported by RFBR-08-02-01360 and Program Presidium RAS "Thermophysics and mechanics of extreme energy effect and physics of strong compressed substance".

[1] V. Dmitriev et al., Journal of Physics and Chemistry of Solids, vol. 64, pp.307-312, 2003. [2] A.P.Kiselev, S.Z.Shmurak, V.V.Sinitsyn, S.S. Khasanov, B.S.Redkin, A.V. Alekseev, Ponyatovsky E.G. Bulletin of RAS:Physics, vol.72, No9, pp.1297-1302, 2008.

**Keywords: high-pressure amorphization, x-ray diffraction**

#### FA2-MS19-P12

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

Coome, C.M. Robertson, J.A.K. Howard, A.E. Goeta  
*Chemistry Department, Durham University, UK.*

E-mail: [m.r.probert@durham.ac.uk](mailto:m.r.probert@durham.ac.uk)

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.

**Keywords:** instrument development, low-temperature crystallography, lasers

#### FA2-MS19-P13

**Phase transition in FeOCl.** Jian Zhang, Alexander Wölfel, Liang Li, Sander van Smaalen. *Laboratory of Crystallography, University of Bayreuth, Germany.*  
E-mail: [zhang.jian@uni-bayreuth.de](mailto:zhang.jian@uni-bayreuth.de)

The crystal structure of the compound FeOCl with the orthorhombic space group  $Pmnm$  was determined by Goldsztaub in 1934 [1]. The magnetic phase transition at  $T_N \approx 80$  K has been studied by several authors [2-4]. Here, we present temperature-dependent X-ray diffraction studies of this transition. With synchrotron radiation, single-crystal X-ray diffraction was performed at beamline D3 of HASYLAB at DESY (Hamburg, Germany). The paramagnetic to antiferromagnetic transition occurs at 79.77 K in our sample, which is on the lower side of the published values. The phase transition is accompanied by a temperature-dependent monoclinic lattice distortion with  $\gamma = 90.079^\circ$  at  $T = 10$  K. The phase transition presumably is of second order with a critical exponent  $\beta = 0.2293(25)$ . Superstructure reflections were found between 10 K and 58 K, which indicate an incommensurate displacive modulation wave accompanying the incommensurate antiferromagnetic order.

[1] Goldsztaub S., *C. R. Acad. Sci. Paris*, 1934, 198, 667. [2] Grant R. W., *J. appl. phys.*, 1971, 42, 1619. [3] Dai Y. D., Yu Z., He Y., *chem. phys. lett.*, 2002, 358, 473. [4] Bannwart R. S., Phillips J. E., Herber R. H., *J. sol. state chem.*, 1987, 71, 540.

**Keywords:** X-ray diffraction, phase transitions

#### FA2-MS19-P14

**Thermomechanical properties of mullite-type Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub> compounds.** Thomas F. Krenzel<sup>a</sup>, Jürgen Schreuer<sup>a</sup>, Manfred Burianek<sup>b</sup>, Manfred Mühlberg<sup>b</sup>, Hartmut Schneider<sup>b</sup>. <sup>a</sup>*Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Germany.* <sup>b</sup>*Institute of Crystallography, University of Cologne, Germany.*  
E-Mail: [thomas.krenzel@rub.de](mailto:thomas.krenzel@rub.de)

Orthorhombic mullite-type Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub> (M = Al<sup>3+</sup>, Ga<sup>3+</sup>, Fe<sup>3+</sup>) compounds doped with divalent cations like Sr<sup>2+</sup> substituting Bi<sup>3+</sup> are supposed to exhibit ion conductivity at elevated temperatures [1]. These compounds are therefore promising candidates for applications in solid oxide fuel cells. The structurally closely related Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub> exhibits multiferroic properties like ferromagnetism and ferroelectricity [2]. Both Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub> are built up from edge-sharing MO<sub>6</sub> and Mn<sub>4</sub>O<sub>6</sub> octahedra forming chains along [001]. In Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub>, they are linked by edge-sharing Mn<sub>3</sub>O<sub>5</sub> square pyramids which alternate with distorted BiO<sub>5</sub> polyhedra in the (001) plane along the *c* axis. In Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub>, neighbored chains are linked by M<sub>2</sub>O<sub>7</sub> dimers. Parallel to [001] the dimers alternate with structural cavities. The stereochemically active 6s lone electron pairs (LEP) of the adjacent Bi<sup>3+</sup> cations point towards the centres of these cavities. Therefore the LEPs stabilise the mullite-type structure of Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub> compounds [3]. In Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub>, however, the cavities are occupied by additional oxygen atoms required for charge compensation reducing the stereochemical activity of the LEPs.

Large single crystals of Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub>, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub> were grown by the top-seeded solution growth method [4]. In order to study their bonding system we determined the single crystal elastic constants of the Bi-mullites from room temperature to 1173 K using resonant ultrasound spectroscopy.

Additionally, the thermal expansion behaviour was investigated in the same temperature range employing dilatometry. For comparison the elastic properties of 2/1-mullite single and polycrystalline samples were studied. The elastic constants decrease continuously with increasing temperature, showing no evidence of any structural instability. However, all compounds display distinct anelastic relaxation peaks near room temperature, probably caused by point defect relaxation processes. The elastic properties of 2/1-mullite compare well with the behaviour of sillimanite, whereas with respect to elastic anisotropy the Bi-containing compounds resemble andalusite.

[1] Zha S., Cheng J., Liu Y., Liu X., Meng G., *Sol. State Ionics*, 2003, 156, 197. [2] Garcia-Flores A.F., Granado E., Martinho H., Urbano R.R., Rettori C., Golovenchits E.I., Sanina V.A., Oseroff S.B., Park S., Cheong S.-W., *Phys. Rev. B*, 2006, 73, 104411. [3] Schreuer J., Burianek M., Mühlberg M., Winkler B., Wilson D.J., Schneider H., *J. Phys. Condens. Matter*, 2006, 18, 10977. [4] Burianek M., Mühlberg M., Woll M., Schmücker M., Gesing T.M., Schneider H., *Cryst. Res. Technol.*, 2009, 44, 1156.

**Keywords:** multiferroic Bi-oxides, structure-physical properties relationships, lone electron pair