

actinide-bearing pyrophosphates and found that all of them exhibit this unusual high temperature behaviour above 673K. Besides we also found that their room temperature structure is not cubic as previously reported [6] but triclinic (distorted cubic) and transform into a cubic form around 150°C. The phase transition has been characterized by various experimental techniques, X-ray diffraction, solid-state NMR and Raman spectroscopy. The room temperature structure has been determined by from synchrotron radiation data obtained at the ESRF. Our presentation will report the experimental results and discussed the structural aspect related with the contraction of the materials at high temperatures.

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**Keywords:** actinides, phosphates

## MS05.P26

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### Crystal Structure and phase transitions of mechanoactivated manganese oxides

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One of the features of the Mn-O system is the formation therein of two Mn<sub>2</sub>O<sub>4</sub> spinel-type polymorphs:  $\gamma$ -Mn<sub>2</sub>O<sub>4</sub> with a spinel structure (sp.gr. *Fd3m*) and  $\beta$ -Mn<sub>2</sub>O<sub>4</sub> with a hausmannite structure (sp.gr. *I4/amd*) often considered as a tetragonally distorted spinel with lattice parameters  $a^* = \sqrt{2} a, < c (c/a^* > 1)$ . The tetragonal distortion of the spinel lattice is due to the cooperative Jahn-Teller effect, and is caused by Mn(III) ions on octahedral sites. Transformation between the two structures is observed both under equilibrium non-ambient conditions (at 1172°C in air) and on quenching the oxide from a high temperature state to room temperature where only a hausmannite structure exists. In this work effects of mechanical activation on the crystal structure and phase transitions of the treated manganese oxides were studied by high-temperature X-ray diffraction.

Highly activated manganese oxides (MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and MnO) were prepared by high-energy ball milling ( $g > 60$ ). The as-prepared mechanically activated manganese oxides were characterized as single-phased, nanoscaled or ultra-fine-grained compounds.

Ball milling gave rise to a direct phase transition from  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> to  $\gamma$ -Mn<sub>2</sub>O<sub>4</sub> omitting  $\beta$ -Mn<sub>2</sub>O<sub>4</sub> phase during heating. This result was obtained both for the as-treated nanoscaled  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> oxide and for the coarse-grained powder after multiple thermal recycling. The same effects were observed upon thermal study of the other activated manganese oxides. A significant increasing in the temperature of the phase transition from Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> during heating and an easier reversibility of the Mn<sub>3</sub>O<sub>4</sub> to Mn<sub>2</sub>O<sub>3</sub> phase transition upon cooling were also detected. It was proposed structural defects due to the mechanical activation are responsible for the anomaly in phase transition behaviour of mechanoactivated manganese oxides. Therefore the structure and microstructure of the phases involved were refined depending on treatment conditions and temperature.

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**Keywords:** oxide, temperature, transition

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### Hybrid instrument for in situ studies at the ESS

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The decision to build the European Spallation Source (ESS) came in the spring of 2009. The ESS will be built in Lund, Sweden and become the most powerful neutron source in the world. The ESS will give unprecedented possibilities for neutron scattering in crystallography and materials science. Investigations of materials at multiple length scales are getting increasingly important for understanding and improving materials performance such as hydrogen storage, solid oxide fuel cells and lithium ion batteries.

A new concept for a neutron scattering instrument will be presented. The new idea combines powder neutron diffraction (PND), small angle neutron scattering (SANS), and neutron imaging (NI) in the same instrument. The PND potentially allows extraction of pair distribution functions for looking at amorphous systems. By combining these techniques it will be possible to look at length scales 0.01-5 nm using diffraction, 1-1000 nm using SANS, and 0.01-100 mm using NI. In addition to the different techniques a high time resolution is envisioned to study processes at the subsecond level. In this way it is possible to study materials *in situ* or *in operandi*.

Through the presentation it is intended to start discussions with the potential user community of the suggested hybrid instrument. The ESS is soon to determine the instrument suite which will be built in the first round. Since this instrument presents new concept there is no existing user community. The IUCr is therefore a great opportunity for engaging with the potential users.

**Keywords:** neutron scattering, materials, in situ

## MS05.P28

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### Negative thermal expansion in trioxane silica sodalite (TRSS)

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The thermal dehydration and template burning process of a silica sodalite (SS), synthesized in the presence of boric acid and trioxane (TR), Na<sub>0.15</sub>[B<sub>0.07</sub>Si<sub>11.93</sub>O<sub>24</sub>]-1.8TR, were studied *in situ* by synchrotron powder diffraction up to 900°C. Time-resolved diffraction data were collected at the GILDA beamline at ESRF (Grenoble). Thermal analyses (TG, DTA and DTG) of the as-synthesized samples were carried out in the same temperature range under a constant flux of air (heating rate 5°/min).

The cell volume of TRSS does not change remarkably until the expulsion of the template, which occurs above 380°C, as inferred by TG analysis weight loss and by the structure refinement of trioxane molecule occupancy. When trioxane molecule decomposition begins, volume expansion becomes negative. This result is unusual for sodalite type materials which typically show positive thermal expansion [1-3]. However, in all these studies the extraframework content is given by cations or anions (such as Cl<sup>-</sup>, F<sup>-</sup>) which cannot be expelled during heat treatment. In our case, extraframework content is represented by organic molecules which are expelled upon heating. A similar result was observed only in a silica sodalite synthesized in the presence of ethylene glycol [4]. These results suggest that when the organic molecules are neutral complex and only act as spacer, a contraction of

the framework occurs upon calcinations, thus explaining the negative thermal expansion.

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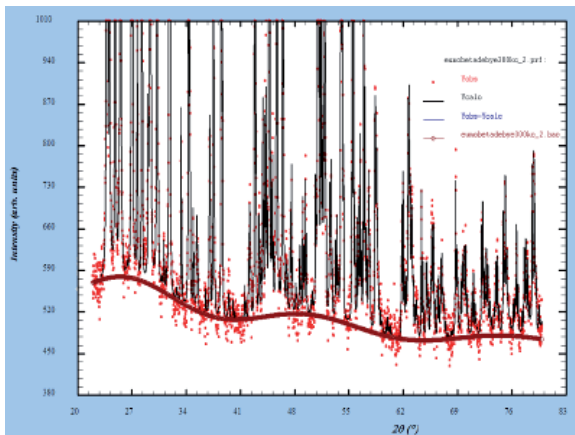
**Keywords:** negative thermal expansion, trioxane silica sodalite, in situ time-resolved diffraction.

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**Structural study of  $\text{Eu}_2(\text{MoO}_4)_3$  and  $\text{Sm}_2(\text{MoO}_4)_3$  polymorphs**  
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Light RE molybdates (RE=La-Eu) can occur in two differently ordered scheelite-type ( $\text{CaWO}_4$ ) structures:  $\text{La}_2(\text{MoO}_4)_3$  [1] and  $\alpha\text{-Eu}_2(\text{MoO}_4)_3$  [2]. Intermediate molybdates (RE=Sm-Ho) show the  $\beta'$ - $\text{Gd}_2(\text{MoO}_4)_3$  ferroelectric-ferroelastic phase [3]. A sound knowledge of the dielectrical and optical properties of  $\text{RE}_2(\text{MoO}_4)_3$  crystals correlated with their crystal structure is of fundamental importance for the application of these materials. Sm and Eu molybdates are particularly interesting because both phases ( $\alpha$  and  $\beta'$ ) are stable at room conditions [4], [5]. In this work, we have studied the evolution of the four phases ( $\alpha$ ,  $\beta'$ ,  $\beta$  and amorphous) of  $\text{Eu}_2(\text{MoO}_4)_3$  and  $\text{Sm}_2(\text{MoO}_4)_3$  with the temperature, in order to explain a new anomaly detected in their dielectric permittivity and in the heat capacity around 275K. Such anomaly can be related with a phase transition between the ferroelectric phase  $\beta'$  and/or to the  $\alpha$  phase, before the ferroelectric( $\beta'$ )-paraelectric( $\beta$ ) transition and the  $\beta$ - $\alpha$  transition at higher temperature. We have applied a new alternative method for treating distorted structures by means of symmetry mode analysis, performed using the program AMPLIMODES, developed in the Bilbao Crystallographic Server [6], and the Rietveld refinement of the amplitudes of such symmetry modes, instead of dealing with the atomic coordinates using the Fullprof program [7]. Moreover, the diffuse scattering has been analyzed and quantified to explain the dielectric and thermal anomalies.



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**Keywords:** rare-earth molybdate, phase transition, polymorphism.

**MS05.P30**

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**Recent developments at the ECHIDNA high-resolution neutron powder diffractometer**  
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The ECHIDNA high-resolution neutron powder diffractometer at OPAL has been in routine and largely trouble-free operation for three years. Data from ECHIDNA have appeared in over 30 publications, covering a temperature range of 1.5K to 1900K and magnetic fields up to 7 T.

ECHIDNA data reduction is largely automated, with a user-friendly interface and a wide choice of output formats (hdf, pdCIF, xyd, GSAS). Data reduction implements a sophisticated approach to gain correction, described in a companion poster [1], and provides large amounts of metadata relating to the data reduction via the pdCIF output format.

The range of instrument configurations continues to expand. A low-temperature (<1K), cryogen-free top-loading cryostat is currently being commissioned and first results are reported. In addition, the maximum takeoff angle has been increased from 140 to 155 degrees without compromising our ability to use the robotic sample loader.

In addition to the regular calls for proposals twice a year, ECHIDNA operates a popular fast access mail-in program. In order to participate, applicants should fill in the simple web-based form accessed via <http://neutron.ansto.gov.au>. Following safety and technical review, applicants forward their samples to us and data are returned typically within one month of sample receipt. Mail-in sample environment is usually restricted to room temperature and/or 4K.

[1] J.R. Hester, "Efficiency correction for neutron powder diffraction area detectors", MS-68

**Keywords:** powder diffraction, instrumentation, neutron

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**High-Pressure Neutron Diffraction Study of  $\text{Fe}_{1.087}\text{Te}$**   
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The crystal and magnetic structures of  $\text{Fe}_{1.087}\text{Te}$  were studied at high pressures and low temperatures. The experiment was performed on the DMC diffractometer at the SINQ spallation source at Paul Scherrer Institut, Switzerland. The sample was loaded into a clamp type pressure-cell using Fluorinert as the pressure transmitting medium. NaCl was used as an internal standard for pressure calibration and the