

[3] Different sets of stacking vectors give non-congruent sets of interatomic distances which yield almost the same Patterson function and hence similar diffraction patterns.

[1] Snyder G. J., Toberer E. S., *Nat. Mater.* **2008**, 7, 105. [2] Schneider M. N., Seibald M., Oeckler O., *Dalton Trans.* **2009**, 2004. [3] Patterson A. L., *Phys. Rev.* **1944**, 65, 195.

Keywords: thermoelectrics; homometry; tellurium compounds¹

FA2-MS04-P08

Temperature- and Concentration-induced Structural Transitions in $\text{Pr}_{1-x}\text{R}_x\text{AlO}_3$. Leonid Vasylechko^a, Tetyana Basyuk^a, Anatoliy Senyshyn^{a,b}, Dmytro Trots^b, Rainer Niewa^c, Stefan Hoffmann^d. ^aDepartment of Semiconductor Electronics, Lviv Polytechnic National University, Lviv, Ukraine. ^bTU Darmstadt, Germany. ^cTU Munich, Germany. ^dMPI CPfS, Dresden, Germany.

E-mail: crystal-lov@polynet.lviv.ua

The pseudo-binary systems PrAlO_3 – RAIO_3 (R = rare earth metals) display complex phase and structural behaviours. Seven different types of crystal structures ranging from the ideal cubic perovskite to its triclinic derivative are found among $\text{Pr}_{1-x}\text{R}_x\text{AlO}_3$ solid solutions, depending on composition and temperature [1]. In this work, the influence of both “chemical pressure” and temperature on the crystal structures of PrAlO_3 -based perovskites and on the character of structural phase transformations occurring in the pseudo-binary systems PrAlO_3 – RAIO_3 is discussed on the basis of *in situ* high resolution powder diffraction applying synchrotron radiation and differential thermal analysis.

At room temperature (RT), continuous solid solutions $\text{Pr}_{1-x}\text{R}_x\text{AlO}_3$ with rhombohedral perovskite structures are formed in the La and Nd systems, whereas in the systems with Sm, Eu and Gd, the phase separation in two solid solutions with LaAlO_3 and GdFeO_3 types of structures occurs. One more kind of solid solution with orthorhombic structure (*Imma*) at RT has been observed in the systems with Ho–Er and Y. At elevated temperatures, orthorhombic and rhombohedral PrAlO_3 -based perovskites undergo structural phase transitions *Pbnm*–*R-3c* and *R-3c*–*Pm-3m*, respectively. Similar to the “pure” aluminates, both transitions can be parameterized in the terms of Goldschmidt tolerance factor. The transition temperatures increase linearly with decreasing average R-cation radii in $\text{Pr}_{1-x}\text{R}_x\text{AlO}_3$ solid solutions.

Much intricate relationship was observed between the cationic substitution and low-temperature (LT) structural transformations *R-3c*–*Imma* and *Imma*–*I2/m* in the PrAlO_3 – RAIO_3 systems. In the systems with La and Nd, the temperatures of both transitions decrease with decreasing Pr content, whereas in the systems with Sm–Tm and Y a decrease of the *Imma*–*I2/m* and an increase of the *R-3c*–*Imma* transition temperatures are observed. The range of existence of the orthorhombic (*Imma*) phase expands in these systems with decreasing Pr content, thus explaining an appearance of this phase in the Ho–Er and Y systems

at RT. Unexpectedly, in the PrAlO_3 – NdAlO_3 system a rare triclinic structure has been found below 70 K, which is the first representative among the perovskites with a single B-cation.

A complicated character of electron-phonon and phonon-phonon coupling is evidently the reason of the anomalous thermal behaviour recently observed in the majority of RAIO_3 perovskites (R=Eu–Dy, Er, Tm, Y) [1]. However, in contrast to PrAlO_3 and CeAlO_3 , in which such a coupling leads to the change of crystal structures at LT, the present anomalies are reflected in the different deviations of the lattice expansion from the “normal” trends.

[1] L. Vasylechko, A. Senyshyn, and U. Bismayer, Perovskite-Type Aluminates and Gallates. In K.A. Gschneidner, Jr., J.-C.G. Bünzli and V.K. Pecharsky, editors: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 39, Netherlands: North-Holland, **2009**, pp. 113-295.

Keywords: perovskite oxides; structural transitions; phase diagrams

FA2-MS04-P09

Hydrogen Storage Materials Studied at Neutron Powder Diffractometer SPODI. Markus Hoelzel^a, Eveline Weidner-Ronnefelder^b, Fransceco Dolci^c, Jianjiang Hu^e, Norbert Juenke^d, Hartmut Fuess^a. ^aFachbereich Material- und Geowissenschaften, Technische Universität Darmstadt, Germany. ^bInstitute for Energy, Joint Research Centre Petten, Netherlands. ^cInstitut für Nanotechnologie, Forschungszentrum Karlsruhe, Germany. ^dInstitut für Physikalische Chemie, Universität Göttingen, Germany.

E-mail: markus.hoelzel@frm2.tum.de

The structure and phase transformation behaviour of promising hydrogen storage materials has been investigated by neutron powder diffraction. In this contribution, we report on measurements carried out at the high-resolution neutron powder diffractometer SPODI (FRM II / Garching n. Munich, Germany) [1]. The instrument provides diffraction patterns with excellent profile shape and high resolution over a wide 2 θ scattering angular range. Thus it suited for structure refinement on complex systems, in particular phase mixtures. On the other hand, the stepwise movement of the detector array limits the possibilities for kinetic studies.

Fully deuterated samples of the system LiD/Mg(ND)_2 have been studied after desorption and re-deuteration at 220 °C and different pressures up to 70 bar to analyse the phase transformation behaviour. The measurements were carried out using a wavelength of 2.536 Å. The analysis of diffraction patterns collected at different deuterium pressure levels revealed that the deuteration occurs via intermediate reaction steps. Corresponding intermediate phases could be identified and analysed by Rietveld refinement.

A sample of $\text{Li}_4(\text{NH}_2)_3(\text{BD}_4)$ was studied at ambient conditions using a wavelength of 1.548 Å. The compound was synthesized by mixing a 1:3 stoichiometric ratio of

LiBD₄ and LiNH₂ precursors. To avoid the high absorption of natural boron, pure ¹¹B was used. The isotopically labeled, mixed H/D sample enabled the determination of D/H occupancies on the four distinct sites. The structure was analysed by Rietveld refinement, proving the space group and revealing H-N-N and D-B-D bond angles and metal – hydrogen atomic distances.

[1] Hoelzel M., Senyshyn A., Gilles R., Boysen H., Fuess H. *Neutron News* 18(4) 2007.

Keywords: hydrogen storage; hydride structure; neutron diffraction

FA2-MS04-P10

Kinetic and Morphological Effects of Biopolymers on the Growth of Hydroxyapatite Crystals. Özlem Doğan^a, Özge Cinel^a, Mualla Öner^a. ^a*Yıldız Technical University, Chemical Engineering Department, Davutpasa 34210 Istanbul, Turkey.*

E-mail: dogano@yildiz.edu.tr

Modelling of the biologic materials require crystallization strategies that provide control over the structure, size and morphology of inorganic crystals. The biological synthesis of inorganic solids often yields materials of uniform size, unusual habit, organized texture and defined structure and composition under moderate conditions of supersaturation and temperature (1, 2). Additives of both organic and inorganic nature play an important role in crystallization processes. They alter the surface properties of the crystals which leads to changes in nucleation and growth (3). The growth of nuclei is affected by adsorption these molecules on the active growth sites (4).

In the present work, the effect of a polysaccharide-based polycarboxylate biopolymers on the crystal growth kinetics of hydroxyapatite was studied by seeding stable supersaturated calcium phosphate solutions with crystals. Carboxymethyl inulin which has a three different number of carboxylate group has been used as additive. The polymer concentration and the carboxylation degree of the polymer were important factors for controlling crystallization.

[1] Öner M., Doğan Ö., *Progress in Crystal Growth and Characterization of Materials*, 2005, 50, 39. [2] Nancollas G.H., Wu W., *J.Crystal Growth* 211, 2000,137. [3] Öner M., Doğan Ö., Öner G., *J.Crystal Growth*, 1998, 186, 427. [4] Lioliou M.G., Paraskeva C.A., Koutsoukos P.G., Payatakes A.C., *J.Colloid and Interface Science*, 2006, 303, 164.

Keywords: hydroxyapatite; biopolymers; crystallization

FA2-MS04-P11

Control of Calcium Oxalate Crystallization by Using Polymeric Additives. Emel Akyol^a, Semra Kirboğa^a, Mualla Öner^a. ^a*Department of ChemicalEngineering, Yıldız Technical University, İstanbul, Turkey.*

E-mail: ekayol@yildiz.edu.tr

Chemical Engineers and urologists have been interested in calcium oxalate crystallization for many years due to its importance on biomineralization and industrial crystallization applications [1,2]. Calcium oxalates are the main components of both pathological deposits in the urinary tract and scale formed on the radiator tubes in evaporators [3,4]. Deposits are desired to remove from the solution in industrial applications since they may reduce the heat transfer efficiency. One common method to inhibit the scale formation is using a suitable additive.

In this study, the effects of acrylic acid and vinylsulfonic acid copolymers on the growth mechanism of the calcium oxalate crystals have been investigated by using spontaneous crystallization method. All polymers tested in this study are effective as growth inhibitors under the experimental conditions. Some of copolymers not only provided the inhibition of calcium oxalate crystallization but also changed the crystal morphology.

[1] Zauner R., Jones A. G., *Ind. Eng. Chem. Res.*, 2000, 39, 2392. [2] Bertherton T., Rodgers A., *Journal of Crystal Growth*, 1998, 192, 448. [3] Akyol E., Öner M., *Journal of Crystal Growth*, 2007, 307, 137. [4] Thongboonkerd V., Semangoen T., Chutipongtanate S., *Clinica Chimica Acta*, 2006, 367, 120.

Keywords: calcium oxalate; additive; crystallization

FA2-MS04-P12

The Phenyl Substitution Effects on the 2,4,6-Triphenoxy-1,3,5-Triazines. Alajos Kálmán^a, Petra Bombicz^a, Nikolett B. Báthori^a. ^a*Institute of Structural Chemistry, Chemical Research Center, HAS, Budapest, Hungary.*

E-mail: akalman@chemres.hu

Semirigid molecules [1] easily form isostructural [2] groups which may then be related via morphotropic steps [3] *i.e.* by virtual non-crystallographic rotations (*ncr*) and/or translations (*nct*) [4]. Occasionally, polymorphs are also formed from isostructural layers or columns [5] via morphotropism. The semirigid molecules of the title compounds [6] prompted us to study the links between their isostructural groups [7]. Revisiting [8] the supramolecular symmetries disclosed for the Piedfort Units (PUs) [9], now we compare the effects of aryl substitution: i) how do the *ortho*, *meta* or *para* functions influence the perfect or relaxed C₃ molecular symmetry and ii) what are the common motives of these structures linked by virtual *ncr*-s and/or *nct*-s.

The *para*-substitutions restore the C₃ axis relaxed in the parent molecule (POT) which crystallizes in space group *Ia*. The columns of the 4-XPOT derivatives are held together by three parallel glide planes in space group *R3c*. Isostructurality of the alkyl row is terminated by the 'Butyl functions. One of the aryl groups rotates through 180° around the O-C(triazine) bond and the molecules crystallize in space group *P2₁/c* [10]. The smallest *halo* function *F* retains the relaxed C₃ symmetry of POT, but every second band of the molecules rotates around the *b* axis by 180°. The glide planes of *Ia* at *y* = ±¼ are converted into centers of inversion in space group *P2₁/c*. Thus POT and 4-FPOT