

movement of a molecule can induce polymorphic transition into a new metastable form.

The study has been supported by a grant from BRHE (RUX0-008-NO-06) and Integration projects 13 & 109 from the SB RAS.

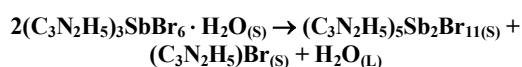
[1] Blagden N., Davey R.J., Lieberman H.F. Williams L., Payne R., Roberts R., Rowe R., Docherty R.J., *J. Chem. Soc. Faraday Trans.*, 1998, 94, 1035. [2] Drebuschak V.A., Drebuschak T.N., Chukanov N.V., Boldyreva E.V. *J. Therm. Anal. Cal.*, 2008, 93, 343. [3] Drebuschak T.N., Chukanov N.V., Boldyreva E.V., *Acta Cryst. C*, 2008, 64, o623. [4] Drebuschak T.N., Chesalov Yu.A., Boldyreva E.V., *Acta Cryst. B*, 2009, 65, 770.

Keywords: phase transitions in solids, drug polymorphism, low-temperature structure

FA4-MS35-P10

Unprecedented solid-state chemical reaction – from $(C_3N_2H_5)_3SbBr_6 \cdot H_2O$ to $(C_3N_2H_5)_5Sb_2Br_{11}$; polymorphism of substrate and products. A. Gagor^[a], A. Piecha^[b], R. Jakubas^[b] and A. Pietraszko^[a]. ^a*Institute of Low Temperature and Structure Research PAS, Wrocław, Poland*, ^b*University of Wrocław Joliot-Curie 14 50-383 Wrocław, Poland*
E-mail: a.gagor@int.pan.wroc.pl

A novel organic-inorganic hybrid material, tris(imidazolium) hexabromoantimonate(III) hydrate, $(C_3N_2H_5)_3SbBr_6 \cdot H_2O$ (abbreviated as TIBA) undergoes an unprecedented *in situ* solid-state chemical reaction above 328 K:



that leads to multiphase crystallites dominated by ferroelectric $(C_3N_2H_5)_5Sb_2Br_{11}$.

The room temperature structure of TIBA consists of discrete $SbBr_6^-$ anions, disordered imidazolium cations, and water molecules forming a 3D array of hydrogen bonds. The solid-state chemical reaction leads from $[SbBr_6]^{3-}$ to $[Sb_2Br_{11}]^{5-}$ chemical stoichiometry of anions. The creation of ferroelectric^[1] crystallites – $(C_3N_2H_5)_5Sb_2Br_{11}$ – in an “annealed” sample of $(C_3N_2H_5)_3SbBr_6 \cdot H_2O$ is confirmed by X-ray diffraction phase analysis, dielectric spectroscopy, and pyroelectric measurements. The dielectric response of the electric permittivity and the critical slowing down of the process observed near 140 K in the “annealed” sample of TIBA are treated as a “fingerprint” of a neat $(C_3N_2H_5)_5Sb_2Br_{11}$ ferroelectric. Furthermore, TIBA undergoes isostructural discontinuous phase transition at 212/221 K (cooling-heating) ($P2_1/c \leftrightarrow P2_1/c$). The phase transition mechanism is characterized by two contributions: an order-disorder (cationic substructure) and a displacive one (water molecules).

Crystal structure of two polymorphs of second product of reaction: $(C_3N_2H_5)Br$ that crystallizes from water solution below 273 K are also presented along with the order-disorder phase transition mechanism.

[1] A. Piecha, A. Pietraszko, G. Bator, R. Jakubas *J. Sol. State Chem.* 2008, 181, 1155-1166

Keywords: ferroelectric, halogenoantimonates(III), phase transitions

FA4-MS35-P11

Topotactic phase transformation of $4H-Cu_yTa_{1-x}S_2$ into $4H-Ta_{1-x}S_2$. Bernd Harbrecht^a, Wenjie Yan^a, Otfried Lemp^a, Steffen Zörb^a, Kirsten Bohnen^b

^a*Department of Chemistry, Philipps University Marburg, Germany*, ^b*present address: Deutsches Museum Bonn, Germany*

E-mail: harbrecht@chemie.uni-marburg.de

Tantalum forms a series of polytypic ternary sulfides of general composition $Cu_yTa_{1-x}S_2$.^[1,2] The layered-type phases are good electronic and ionic conductors. The mobile Cu ions (y) and excess Ta (x) are inserted in spatially separated van der Waals gaps of a layered TaS_2 host structure the type of which depends upon x, y and T. Oxidative deintercalation of Cu with iodine affords new polymorphs of $Ta_{1-x}S_2$. The new polymorphs differ from those accessible from the elements at temperatures above 1250 K by higher order staging, i.e. excess Ta (x) is not found in all van der Waals gaps what confers lubricant-like properties to these Ta-rich disulfides. Such polytypes can be classified by a code nN in which n counts the number of TaS_2 slabs in the repeat unit and N refers to the lattice symmetry, e.g., H for hexagonal. Here, we present the structure of a ternary 4H polytype that - upon progressive deintercalation of Cu at ambient temperature - topotactically transforms into a differing 4H polytype. The transition is reflected in divergent X-ray diffractograms showing an offset of the reflections and a drastic change in the intensity modulation of h0l zonal reflections. Structural features of the two polymorphs derived from the distinctive intensity modulations are highlighted and discussed in the light of known polymorphs. Electronic and mechanistic aspects of the transformation are discussed.

[1] Harbrecht B., Kreiner G., *Z. anorg. Allg. Chem.*, 1989, 572, 47-54.

[2] Kirsten Bohnen, Dissertation, Universität Bonn 1995.

Keywords: transition metal dichalcogenides, polytypes, topotactic phase transformation

FA4-MS35-P12

Elucidation of Crystallization Processes – The Polymorphism of Nifedipine. Maria Klimakow^a, Klaus Rademann^b, Franziska Emmerling^a, ^a*BAM Federal Institute for Materials Research and Testing, Berlin, Germany*, ^b*Humboldt-University Berlin, Germany*

E-mail: maria.klimakow@bam.de

The crystallization process of the polymorphic compound nifedipine (4-(2-nitrophenyl)-2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine, $C_{17}H_{18}N_2O_6$) using different solvents was investigated *in situ* by X-ray diffraction and Raman spectroscopy. In medical treatments, nifedipine acts as dihydropyridine calcium antagonist. Despite the pharmaceutical importance, the wide use of the substance, as well as knowledge of its polymorphism, the crystal structures of most of the nifedipine polymorphs still remain unknown. To investigate the formation of intermediate phases, which are kinetically favored and formed preferentially under fast evaporation conditions, an acoustic levitator was employed as sample environment for the combination of time-resolved X-

ray diffraction and Raman spectroscopy (simultaneous data acquisition within a 20 seconds period) [1]. This setup provides a contactless sample positioning and eliminates the influence of solid container walls. In addition, it enables *in situ* monitoring of solutions during evaporation of the solvent (methanol, ethanol, acetone, dichloromethane, and acetonitrile) over a concentration range of three orders of magnitude. These real time measurements allow the determination of the phase content from the onset of the first crystalline molecular assemblies to the stable system. The results indicate the existence of solvent dependent transient phases during the crystallization process. The quality of the data allowed the assignment of the lattice constants of the hitherto unknown crystal structure of the β -polymorph. In the final stage the fast evaporating solvents always led to the formation of the α -polymorph. Using the slow evaporating solvent dimethyl sulfoxide (DMSO), a novel pseudo-polymorph was observed. Its crystallization process was followed by means of light microscopy and ESEM coupled with EDS analysis. The single-crystal X-ray structure of the solvated species nifedipine · DMSO (1:1) is reported for the first time [2]. With the results of the presented investigation, a tool for studies on polymorphic transition mechanisms and the influence of solvents on these processes is provided.

[1] Klimakow, M., Leiterer, J., Kneipp, J., Rössler, E., Panne, U., Rademann, K., Emmerling, F., *Langmuir* 2010, la100540q. [2] Klimakow, M., Rademann, K., Emmerling, F., *Crystal Growth & Design* 2010, submitted

Keywords: polymorphism, nifedipine, synchrotron radiation

FA4-MS35-P13

Structural crystal-to-crystal phase transitions in 1,4-diaminium bis(dichloroacetate) Maciej Kubicki^a,

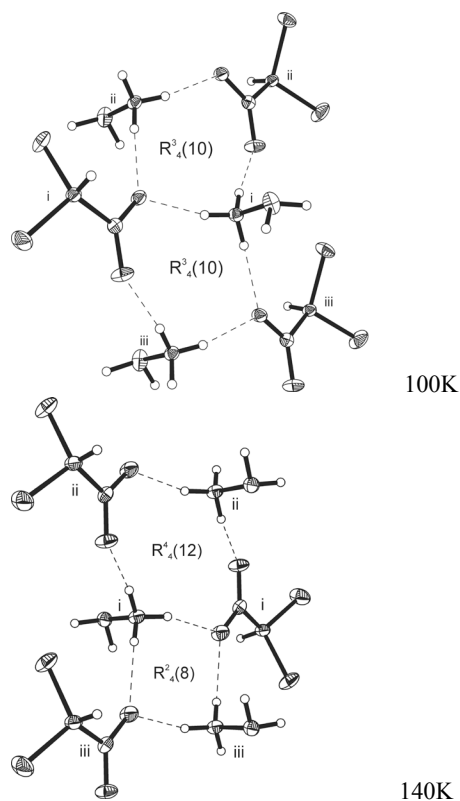
Agnieszka Paul^{a,b}, Marek Szafranski^a

^aAdam Mickiewicz University in Poznań, Poland

^bNancy University, CNRS, France

E-mail: mkubicki@amu.edu.pl

Crystals of putrescinium bis(dichloroacetate), $(C_4H_{14}N_2)^{2+} \cdot 2C_2HCl_2O_2^-$ undergo two reversible phase transitions between 100 and 295K. The first transition occurs about 140K, and the second one around 249K. The low temperature structure (α -phase) is best described in $P2_1/c$ space group. The transition to $I2/a$ space group (β -phase) involves the doubling of one of the unit-cell parameters. The second phase transition recovers the initial $P2_1/c$ symmetry (α' -phase). Only in the low-temperature α -phase the putrescinium dication is disordered across the inversion center (in other phases it is ordered), while the disorder of the anion occurs always for the temperatures close to the phase transitions. It looks like the disordering of the anion starts the sequence of changes which eventually cause the change of the phase. The hydrogen bond networks are similar, but some essential changes occur. Using graph-set method, the hydrogen bond patterns are built from the same motifs for α and α' phases, whereas for the β -phase these "building blocks" are different, for instance the typical for diaminium salts $R^2_4(8)$ ring occurs.



Despite these differences, the layer structure is present in all three phases. The additional calorimetric and dielectric data were collected in order to help in the description of the process of phase change. Also the Hirshfeld surfaces were used to better visualize the changes.

Keywords: phase transitions; hydrogen bonds; putrescinium

FA4-MS35-P14

Solid state transition in $[Cd(\mu-Br)_2(py)_2]_\infty$. Kevin Lamberts^a, Ulli Englert^a, ^aInstitute of Inorganic Chemistry, RWTH Aachen University, Germany
E-mail: Kevin.Lamberts@rwth-aachen.de

Earlier research on halide-bridged Cd(II) coordination polymers with axial pyridine ligands indicated a phase transition around 180 K for $[Cd(\mu-Br)_2(py)_2]_\infty$ [1]. It is remarkable that this crystal-to-crystal transition seems to be fully reversible. The room temperature structure has already been determined [2] but the low temperature phase and the transition itself still have to be analysed more precisely.

Task of the work is the concrete determination of the twinned low temperature phase of $[Cd(\mu-Br)_2(py)_2]_\infty$ and the specification of the phase transition. For the crystal structure determination the group-subgroup relationship is of particular interest. In connection with the phase transition the exact transition point is going to be specified and its thermodynamic conditions will be assayed. For these purposes single crystal X-ray diffraction, powder diffraction and differential scanning calorimetry will be used.

Another point of interest is the structure similarity of the low temperature phase with chemically related complexes and the effect of mixed crystals on the phase transition.