

**FA4-MS01-P01**

**Barium Ternary Fluorides  $BaMF_4$  ( $M = Mn, Zn,$  or  $Mg$ ) at Non-ambient Conditions.** Jose Maria Posse<sup>a</sup>, Andrzej Grzechnik<sup>a</sup>, Karen Friese<sup>a</sup>. <sup>a</sup>*Dept. of Condensed Matter Physics, University of the Basque Country, Bilbao, Spain.*

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The compounds  $BaMF_4$  ( $M = Co, Fe, Mn, Ni, Zn,$  or  $Mg$ ) crystallize in space group  $Cmc2_1$  ( $Z = 4$ ) at ambient conditions. The cation  $M$  is surrounded by six fluorine atoms forming an irregular octahedron. Four of the octahedra are connected via common corners with others, generating puckered layers perpendicular to the  $b$  axis. The neighbouring layers are shifted with respect to each other by a translation of  $a/2$ . The barium atoms are located in the interlayer spaces [1]. These compounds are interesting due to the fact that some of them ( $M = Mn, Fe, Co,$  or  $Ni$ ) exhibit a multiferroic behaviour [2].  $BaMnF_4$  has a second-order phase transition to an incommensurate phase at low temperatures ( $T \sim 250$  K) supposedly with superspace group  $C2_1(\frac{1}{2} \frac{1}{2} \gamma)$  [3]. In addition, it exhibits magnetic anomalies at about 50 K and 27 K, the latter being due to a formation of an antiferromagnetic phase [4].

The aim of our study is to examine the structural instabilities [5] in  $BaMnF_4$ ,  $BaZnF_4$  and  $BaMgF_4$  at low temperatures and high pressures.

Powder x-ray diffraction (ID31 beamline, ESRF) and single-crystal x-ray diffraction (SCD beamline, ANKA; our laboratory in Bilbao) experiments were carried out on  $BaMnF_4$ ,  $BaZnF_4$  and  $BaMgF_4$  from 290 K to 10 K at atmospheric pressure. Both  $BaZnF_4$  and  $BaMgF_4$  do not undergo any phase transitions at low temperatures. On the other hand, our diffraction data on  $BaMnF_4$  indicate that it transforms to an incommensurate monoclinic phase which is affected by twinning. In contrast to the earlier investigations [3], our data indicate the superspace group  $X2_1(\frac{1}{2} \frac{1}{2} \gamma)$  with  $X = (\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$  as the correct choice. Upon lowering the temperature, the  $\gamma$  component of the modulation wave vector increases and reaches a constant value  $\gamma \approx 0.3948$  below 50 K, i.e., in the temperature range in which the magnetic anomalies occur [4].

We also performed high-pressure measurements using single-crystal x-ray diffraction in our laboratory and in HASYLAB/Hamburg ( $BaZnF_4$  and  $BaMgF_4$ ) as well as Raman spectroscopy ( $BaZnF_4$ ). The Raman data suggest pressure-induced phase transition in  $BaZnF_4$  at about 5 GPa. Currently, we are analyzing our diffraction data to elucidate the high-pressure structures of  $BaMgF_4$  and  $BaZnF_4$ . Our intention is to perform high-pressure single-crystal diffraction experiments to examine the structural behaviour of  $BaMnF_4$ .

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**Keywords:** multiferroic; modulated structure; high pressure

**FA4-MS01-P02**

**Modulated Structures in Aluminate Sodalites.** Wulf Depmeier. *Institute of Geosciences, University of Kiel, Kiel, Germany.*

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Aluminate sodalites  $[M_8(XO_4)_2][Al_{12}O_{24}]$ -SOD, with  $M = Ca^{2+}$  or  $Sr^{2+}$ , and  $X = S^{6+}, Cr^{6+}, Mo^{6+}, W^{6+}$ , usually undergo phase transitions from a cubic high temperature phase to one or several non-cubic low temperature, often ferroelastic or ferroelectric, phases. The majority of the low symmetry phases can be described as modulated phases. Commensurately and incommensurately modulated phases with dimensions of the superspace varying between (3+1) and (3+3) have been found. Even small disturbances lead to quite complicated  $T - x$  phase diagrams. The reason for the occurrence of the modulations is believed to be due to the fact that the structure of sodalites in general can be broken down into three partial structures, viz. i) the sodalite framework, ii) an interpenetrating net of cations, and iii) cage anions at the centres of the sodalite cages. In the case of tetrahedral cage anions competitive interactions occur between these partial structures. The system is frustrated and its free energy can be lowered by a modulation. Cascades of phase transitions especially in the Ca-bearing members of the aluminate sodalite family can be rationalized by the fact that the phase transitions from the cubic phase usually happen at the N-point of the body-centred Brillouin zone meaning that the corresponding order parameter has six components. In real space the cascades can be rationalized by interplay of rotational and translational potentials becoming subsequently deeper or shallower as a consequence of the above-mentioned interactions. Chaotic phases and phases due to sliding of modulation waves are anticipated as well.

**Keywords:** sodalites; modulated phases; phase transitions

**FA4-MS01-P03**

**Molecular Structure of 4-(9-Anthryl)-1-phenylspiro[azetidine-3,90-xanthen]-2-one.** İsmail Çelik<sup>a</sup>, Mehmet Akkurt<sup>b</sup>, Aliasgar Jarrahpour<sup>c</sup>, Edris Ebrahimi<sup>c</sup>, Orhan Büyükgüngör<sup>d</sup>. <sup>a</sup>*Department of Physics, Faculty of Arts and Sciences, Cumhuriyet University, 58140 Sivas, Turkey.* <sup>b</sup>*Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey.* <sup>c</sup>*Department of Chemistry, College of Sciences, Shiraz University, 71454 Shiraz, Iran.* <sup>d</sup>*Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey.*

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The  $\beta$ -lactam ring of the title compound,  $C_{35}H_{23}NO_2$ , is nearly planar with a maximum deviation of 0.003 (3) Å from the

mean plane. It makes dihedral angles of 17.4 (2), 85.22 (17) and 65.39 (16)°, respectively, with the phenyl, xanthen and anthracene ring systems. In the crystal structure, there are intramolecular C—H...O and C—H...N contacts and molecules are also linked by C—H... $\pi$  interactions.

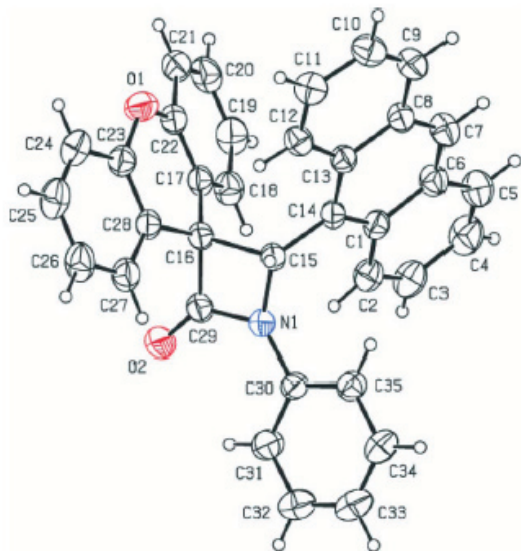


Fig 1: The molecular structure of title compound

The title compound,  $C_{35}H_{23}NO_2$ , crystallizes in the monoclinic  $P2_1/c$  space group with  $a = 13.6906$  (8) Å,  $b = 13.3085$  (7) Å,  $c = 17.3527$  (10) Å,  $\beta = 127.548$  (4)°,  $V = 2506.7$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.08\text{mm}^{-1}$ ,  $R = 0.051$ ,  $wR = 0.110$ ,  $S = 0.90$ .

**Keyword:** crystal structure; 4-(9-Anthryl)-1-phenylspiro[azetidine-3,90-xanthen]-2-one; the  $\beta$ -lactam ring

#### FA4-MS01-P04

**Concentration Modulations and Short-Range vs. Long-Range Order in Layered Tellurides.** Oliver Oeckler<sup>a</sup>, Matthias N. Schneider<sup>a</sup>. <sup>a</sup>Department of Chemistry and Biochemistry, LMU Munich.

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Multinary tellurides have received much attention both as phase-change alloys for data storage and as promising thermoelectrics.[1,2] In the systems  $M\text{-Y-Te}$  ( $M = \text{Ge, Sn, Pb, Ag, In, ...}$ ;  $Y = \text{Sb, Bi}$ ) thermodynamically stable phases are found on pseudobinary lines  $(M\text{Te})_n(\text{Y}_2\text{Te}_3)_m$  and  $(\text{Y}_2\text{Te}_3)_m(\text{Y}_2)_k$ , they exhibit rocksalt-type as well as  $A7$ -type building blocks and can exhibit extremely long translation periods.

Quenching and subsequent annealing yields series of trigonal metastable phases  $(M\text{Te})_n(\text{Y}_2\text{Te}_3)_m(\text{Y}_2)_k$  with building blocks from both types of stable compounds. [3] Although long-periodic order is evidenced by sharp superstructure reflections, pronounced positional disorder is present. Single-crystal X-ray analysis as well as TEM show that the element concentrations vary continuously along the stacking direction of hexagonal atom layers.

Typical examples include  $(\text{Ge}_x\text{Sb}_{1-x/2})_2\text{Te}_3\text{:}[(\text{GeTe})_y\text{Sb}_{1-2y}]_8$  ( $x = 0.31$ ,  $y = 0.0325$ ;  $R\text{-}3m$ ,  $a = 4.266$ ,  $c = 75.02$  Å,  $R1 = 0.051$ ) and  $\text{Ge}_{2-x}\text{Sb}_{2+x}\text{Te}_2\text{Sb}_8$  ( $x = 0.43$ ;  $R\text{-}3m$ ,  $a = 4.258$ ,  $c = 97.23$  Å,  $R1 = 0.044$ ). This variation can be described as a long-range ordered occupational modulation which blurs the boundaries between “building blocks”. Quenching obviously leads to partial spinodal decomposition involving wavy concentration fluctuations. These “waves” are perfected by short-range diffusion during annealing, whereas decomposition is impossible as it requires long-range diffusion. Incommensurate concentration modulations have also been observed.

If the basic structure is close to cubic, e. g. in  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)$  ( $x \geq 3$ ), high-temperature phases with disordered rocksalt-type structures are sometimes observed. Superstructure formation (i. e. either concentration waves or block formation) upon cooling consequently involves multiple twinning. Strain can impede this ordering, resulting in pseudocubic crystals with remarkable diffuse scattering; the maxima coincide with the positions of the strongest superstructure reflections of the corresponding long-range ordered (meta-)stable phases.

Concerning metastable crystalline phases of phase-change alloys, disordered cubic rocksalt-type structures are often assumed.[1] Investigations on comparable bulk samples (e. g. with compositions  $\text{Ge}_{0.73}\text{Sb}_{0.20}\text{Te}$  or  $\text{Ge}_{0.57}\text{Sb}_{0.34}\text{Te}$ ) evidence that pronounced short-range ordering matches with small (distorted) cutouts of the corresponding stable phases. This leads to the hypothesis that metastable crystalline samples may contain twinned and strained nanoscale domains of stable compounds and long-range order is impeded by the stress associated with volume change resulting from partial superstructure formation.

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**Keywords:** phase-change technology; modulated structures; tellurium compounds

#### FA4-MS01-P05

**The Modulated Structure of  $\Lambda$ -Co(Sepulchrates)-Trinitrate at  $T = 100$  K.** Andreas Schönleber<sup>a</sup>, Sander van Smaalen<sup>a</sup>, Wolfgang Morgenroth<sup>b</sup>, Finn Krebs Larsen<sup>c</sup>. <sup>a</sup>Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany. <sup>b</sup>Institute of Geosciences, University of Frankfurt, Frankfurt am Main, Germany. <sup>c</sup>Department of Chemistry, University of Aarhus, Aarhus, Denmark.

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$\Lambda$ -Co(sepulchrates)-trinitrate,  $C_{12}H_{18}N_8Co^{3+} \cdot 3(NO_3)^-$  crystal-lizes at room temperature in symmetry  $P6_322$  [1]. Sepulchrates is (*S*)-(1,3,6,8,10,13,16,19-octa-azabicyclo-[6.6.6]eicosane). The cation and two of the nitrate anions are centred on three fold rotation axes, linked to each other by  $N\text{-H}\cdots\text{O}$  hydrogen bonds. The third nitrate anion is centred on the intersection of the two fold rotation axes and shows orientational disorder.