

PS11.05.02 STRUCTURE INVESTIGATIONS OF $\text{Rb}_2\text{Li}_4(\text{SeO}_4)_3 \cdot 2\text{H}_2\text{O}$ CRYSTALS. Wiesława Bronowska¹ and Adam Pietraszko², ¹Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, ²Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, Poland

In recent years, much attention has been devoted to the two-component systems of the $\text{Li}_2\text{SO}_4 - \text{Me}_2\text{SO}_4$ type, where $\text{Me} = \text{Rb}, \text{Cs}, \text{K}, \text{NH}_4$, as a consequence of the wide range of their physico-chemical properties. An interesting feature of these compounds is the existence of successive phase transitions between their different phases. In part, scientific interest in these systems is motivated by the desire to compare the structural and physical properties of these compounds and to investigate how their feature may be influenced by the structural characteristic.

This paper reports the X-ray powder and single crystal diffraction results obtained for the two-component crystals, $\text{Rb}_2\text{Li}_4(\text{SeO}_4)_3 \cdot 2\text{H}_2\text{O}$, which belong to a new family of selenates hydrates. Crystals were obtained by evaporation of a saturated solution. These crystals have a monoclinic symmetry, (space group $\text{P}2_1/\text{c}$), with two chemical units forming the room temperature unit cell. Lattice parameters at room temperature are the following: $a = 5.256(1)\text{Å}$, $b = 5.178(1)\text{Å}$, $c = 26.739(5)\text{Å}$, $\beta = 93.11(3)\text{deg}$; $V = 726.6(2)\text{Å}^3$. The final discrepancy factor is $R = 0.042$ for $1272F_o > 4\sigma(F_o)$. The refinements of the crystal structure of $\text{Rb}_2\text{Li}_4(\text{SeO}_4)_3 \cdot 2\text{H}_2\text{O}$ have shown that oxygen atoms of a crystal-line water statistically occupy two different positions. The presence of the water molecules in the crystal structure has been confirmed by the infrared measurements. The powder diffraction measurements were performed over the temperature range from 30K to 300K.

PS11.05.03 RECENT ADVANCES IN SEMI-PHENOMENOLOGICAL APPROACH TO STATISTICAL DESCRIPTION AND STABILITY ANALYSIS OF CRYSTAL STRUCTURES. Vladimir N. Bugaev, Roman V. Chepulsii, Dept. of Solid State Theory, Inst. for Metal Physics NAS of Ukraine, Kiev-142, 252180, Ukraine

The brief survey of recent results obtained by the authors on statistical thermodynamic semiphenomenological description of substitutional and interstitial crystal structures is quoted. The generalized lattice gas model is proposed taking into consideration the lattice distortions and many-body interactions [1].

The symmetry properties of interatomic lattice potentials (as in real as in reciprocal space), their changes due to the phase transitions and displays at formation of the structure and thermodynamics of crystal are considered [1,2]. The noncentrality of the pairwise interactions is studied [2].

The complete list of all types of thermodynamically stable (Lifshitz) ordered structures arising from the disordered state of f.c.c., b.c.c. [3] and hexagonal [4] binary solid solutions is obtained.

The possible types of the symmetry-conditioned structural instability channels are considered.

New, vacancy-induced, mechanism of concentrational polymorphism in interstitial alloys is proposed [5].

[1] V. N. Bugaev & R. V. Chepulsii. Acta Cryst. (1995) **A51**, N7, p.456.

[2] V. N. Bugaev & R. V. Chepulsii. Acta Cryst. (1995) **A51**, N7, p.463.

[3] V. N. Bugaev & R. V. Chepulsii. Phys.Stat.Sol. (b) (1995) **192**, N1, p.9.

[4] V. N. Bugaev & R. V. Chepulsii. Acta Cryst. (1996) **A52**, in print.

[5] V. G. Gavrilink, V. N. Bugaev et al. Scr. Metal. (1996), in print.

PS11.05.04 THE MONOCLINIC-TETRAGONAL PHASE TRANSITION AND TUNNEL ION ORDERING IN CESIUM SUBSTITUTED BARIUM MAGNESIUM HOLLANDITES. Robert W. Cheary and Nirmala Maharaj. Department of Applied Physics, University of Technology Sydney, Broadway, New South Wales, Australia 2007.

We have investigated the substitution of Cs for Ba in $\text{Ba}_x\text{Mg}_y\text{Ti}_{8-x}\text{O}_{16}$ as part of a research program to understand the stability of the hollandite structure when loaded with simulated radioactive waste. The general composition of the substituted material is $(\text{Ba}_{1-\beta}\text{Cs}_\beta)_x \text{Mg}_y\text{Ti}_{8-y}\text{O}_{16}$ where $y = x[1 - \beta/2]$ and x is the number of the Ba and Cs per unit cell located in the tunnels sites of the structure. In these hollandites the tunnel sites are not fully occupied, and the Ba and Cs along with the vacant sites can adopt different ordered configurations along the tunnels depending on the occupancy level $x/2$. When this occurs superlattice lines appear in the X-ray powder pattern. The transition from order to substitutional disorder occurs either when the temperature is raised, or when the concentration of Cs is increased. The superlattice lines also display line broadening, through the formation of anti-phase domains, which increases with Cs concentration. Ba hollandites also undergo a distortional transition from a high temperature tetragonal phase to a low temperature monoclinic phase. In pure Ba hollandites this transition can occur at temperatures as high as 500°C depending on the tunnel occupancy. When Cs is introduced into the tunnels the transition temperature is reduced dramatically and beyond $\beta \approx 0.15$ the transition temperature is below room temperature for all occupancies. In this paper we have investigated the ordering of the tunnel ions and the monoclinic-tetragonal phase transition using X-ray diffraction data collected with a Siemens D5000 powder diffractometer fitted with a high temperature stage. The particular aspects reported include;

- the compositions that form when Cs is substituted into barium magnesium hollandite over the known range of stable occupancies ($x = 1.14$ to 1.33) and at increasing levels of Cs from $\beta = 0$ to 0.3 ,
- the changes in lattice parameters, long range order parameter and superlattice line breadth with Cs concentration,
- the effect of temperature on both the ordering and the lattice parameters at different Cs concentrations.

PS11.05.05 THE STRUCTURE OF $\beta\text{-Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$. S. Faulk, P. Calkins and S.M. Haile, Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195 USA

Solid solution studies in the $\text{CsHSO}_4\text{-CsH}_2\text{PO}_4$ system carried out in a search for compounds with unique hydrogen-bonding schemes and related phase transitions, yielded the compound $\beta\text{-Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$. The compound appears to be a disordered form of $\alpha\text{-Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$ recently reported by this group. The β -form crystallizes in space group $\text{C}2/\text{c}$ and has lattice parameters $a = 20.04(1)$, $b = 7.854(5)$, $c = 8.954(5)\text{Å}$ and $\beta = 100.11(2)^\circ$. In comparison, the α form crystallizes in space group $\text{P}2_1/\text{n}$ and has the following lattice parameters: $a = 19.546(3)$, $b = 7.8798(10)$, $c = 9.1854(17)\text{Å}$ and $\beta = 100.536(14)^\circ$. The arrangement of Cs^+ , SO_4^- , and PO_4^- ions are virtually identical in the two forms $\text{Cs}_3(\text{HSO}_4)_2(\text{H}_2\text{PO}_4)$: both exhibit "zig-zag" chains of hydrogen-bonded XO_4 groups (where $\text{X} = \text{P}$ or S), alternating with chains of Cs ions. The XO_4 chains are, in turn, cross-linked to form a three-dimensional framework. The difference between the two polymorphs lies in the absence of the c-centering symmetry in the α form that is present in the β form. Accordingly, the number of atoms in the asymmetric unit of the α form is almost double that of the latter. In particular, in the

C2/c space group, two pairs of oxygen atoms in the vicinity of a single hydrogen bond are related by a center of symmetry. The result is a rather diffusely located proton, distributed over four oxygen atoms in the high symmetry space group, whereas it is localized to the vicinity of two oxygen atoms in the low symmetry space group. The consequences of such a "distributed" proton are evident in the rather long O-O distances. The influence of this local hydrogen-bonding geometry on phase transitions is discussed.

PS11.05.06 PHASE TRANSITION BETWEEN MICROEMULSION AND LAMELLAR PHASE IN AMPHIPHILIC SYSTEMS. S. K. Ghosh, J. Matsuba, S. Komura*, H. Seto*, T. Takeda*, M. Hikosaka*, Graduate School of Biosphere Science, *Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739, Japan

Amphiphiles are intriguing materials that exist in various forms in water-amphiphile binary systems or in water-oil-amphiphile ternary systems. Phase diagram of ternary system involving non-ionic amphiphile "C₁₂E₅/n-octane/water" has been presented by Kahlweit [1]. At equal volume fraction of octane and water with more than 15% volume fraction of amphiphile there are two microemulsion phases that are intervened by a lamellar phase with rising temperature. In order to study the first order phase transition between the microemulsion and lamellar phases we have measured small-angle X-ray scattering intensity from this system extensively. We observed a respective single peak from each of the two microemulsion phases and the lamellar phase. In the temperature ranges between the lamellar and the two microemulsion phases, we also observed a coexistence of two peaks.

These two peaks show a very systematic gradual change with respect to the peak positions q_l and q_m (l and m refer to the lamellar and the microemulsion phases, respectively) and the peak intensities I_l and I_m , as follows. As the temperature is increased from the lower microemulsion phase up to the lamellar phase, I_m decreased and disappeared, while I_l appeared and increased. Simultaneously both q_l and q_m decreased. As the temperature is further increased from the lamellar phase up to the upper microemulsion phase, a similar but opposite systematic change was observed. These behaviors are qualitatively in agreement with what is expected from the *lever rule* in the phase diagram.

We have explained the transitions between the lamellar and microemulsion phases on rising temperature, as a result of the change of spontaneous curvature of the interface film made of amphiphile and subsequent change of *bending elastic energy* within the interfacial model of Andelman et al [2].

1. M. Kahlweit et al., *J. Colloid and Interface Science*, **118** (1987) 436
2. D. Andelman et al., *J. Chem. Phys.* **87** (1987) 7229

PS11.05.07 X-RAY STUDIES OF MAGNETICALLY INTERESTING COMPOUNDS IN THE TEMPERATURE RANGE 10-300K. A. E. Goeta, R. C. B. Copley, C. W. Lehmann, J. A. K. Howard, University of Durham, Durham Chemical Crystallography Group, UK

We present here an application of low temperature crystallography to the study of structure/property relationships. Two systems previously reported to show magnetic phase transitions at approximately 36K and 23K have been investigated using the Fddd high intensity cryogenic diffractometer at Durham, UK.

(i) [*p*-CNSSN·C₆F₄CN]₂. The β-phase of this compound is the first purely organic material to exhibit spontaneous magnetisation above liquid helium temperatures. The compound crystallises in the orthorhombic space group Fdd2 and keeps the same symmetry from room temperature down to 10K. The observed magnetic behaviour has been explained in terms of a phase

transition, at the unprecedentedly high temperature of 36K, from a one-dimensional antiferromagnetic state to a weak ferromagnetic state. The fact that the structure remains in a non-centrosymmetric space group is a very positive finding since it is in accordance with the weak ferromagnetic signal postulated to result from the Dzyaloshinsky-Moriya interaction.

(ii) [(T⁵-Cp*)Cr(T⁵-P₃)Cr(T⁵-Cp*)](SbF₆) A previous SQUID investigation on this triple-decker compound showed it to undergo a spin crossover at approximately 23K. The diffraction study carried out clearly shows a sharp and non-destructive structural phase change at 21K and initial analysis of the full and extensive data suggests that the Cr-Cr separation has shortened from 3.1Å at room temperature to 2.7Å at 12K. This is a first and is seen as clear and exciting experimental evidence for the spin pairing of the chromium atoms.

PS11.05.08 THALLIUM (I) ORTHOFLUORBERILLATE González-Silgo, C.^a, Ruiz-Pérez, C., Martínez-Sarrión, M. L.^b, Mestres L., Solans, X.^c ^aDpto. Física Fundamental y Experimental, Universidad de La Laguna, Spain, ^bDpto. Química Inorgánica, ^cDepto. Cristallografía, Mineralogía y Depositos Minerales Universitat de Barcelona, Spain.

(NH₄)₂BeF₄ and Tl₂BeF₄, with similar ion radii from Rb⁺, are isostructural in Pnam space group. The first shows undergoes two phase transition at lower temperature and crystal structure of Tl₂BeF₄ isn't reported, but it isn't known phase transition. Otherwise, Thallium oxisalts, some of them show structural instabilities, has been lately studied and may be inferred two types of cation with 11 and 9 surrounding O atoms and the importance of the shortest bonds. The structural determination is important to access the role of the atoms placed in large cavities like a particular result of the general rule pointed out I.D. Brown (1992). Tl₂BeF₄ was obtained via reaction BeF₂+H₂F₂+Tl₂CO₃=Tl₂BeF₄+CO₂+H₂O. Mixed crystal were obtaining mixing aqueous solution of (NH₄)₂BeF₄ and Tl₂BeF₄ thermostating at 30C. We have determined the structure of Tl₂BeF₄ and Tl_{1.84}(NH₄)_{0.16}BeF₄: orthorhombic, Pnam, Z=4, a=7.679(2), 7.689(2), b=10.383(3), 10.398(3), and c=5.871(2), 5.886(2). We have found differences between the crystals at room temperature: 1st) In Tl₂BeF₄, a BeF₄ group deformation mainly along b direction and one Be-F bond is near to parallel a axis. 2nd) The arrangement of 11-coordinated cation is similar in both compounds, but the linkage of 9-coordinated cation indicates this (NH₄)⁺ ion plays the most important role in (NH₄)₂BeF₄ phase transition. 3rd) Bond-Valence model predicts structural instabilities in (NH₄)₂BeF₄ while Tl₂BeF₄ is more stable.

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