PS11.05.02 STRUCTURE INVESTIGATIONS OF $Rb_2Li_4(SeO_4)_3 \cdot 2H_2O$ CRYSTALS.

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In recent years, much attention has been devoted to the two-component systems of the Li_2SO_4 - Me_2SO_4 type, where *Me* = Rb, Cs, K, 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, $Rb_2Li_4(SeO_4)_3 \cdot 2H_2O$, 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 $P2_1/c$), with two chemical units forming the room temperature unit cell. Lattice parameters at room temperature are the following: $a = 5.256(1)$Å, $b = 5.178(1)$Å, $c = 26.739(5)$Å, $\beta = 93.11(3)$deg; $V= 726.6(2)$Å^3. The final discrepancy factor is $R = 0.042$ for $1272F_o > 4\sigma(F_o)$. The refinements of the crystal structure of $Rb_2Li_4(SeO_4)_3 \cdot 2H_2O$ have shown that oxygen atoms of a crystalline 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.

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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. Chepulskii. Acta Cryst. (1995) **A51**, N7, p.456.
[2] V. N. Bugaev & R. V. Chepulskii. Acta Cryst. (1995) **A51**, N7, p.463.
[3] V. N. Bugaev & R. V. Chepulskii. Phys.Stat.Sol. (b) (1995) **192**, N1, p.9.
[4] V. N. Bugaev & R. V. Chepulskii. 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.

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We have investigated the substitution of Cs for Ba in $Ba_xMg_xTi_{8-x}O_{16}$ 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 $(Ba_{1-ß}Cs_{ß})_x\, Mg_yTi_{8-y}\, O_{16}$ where $y = x[1 - ß/2]$ 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 $ß \approx 0.15$ 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 ß = 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 β-$Cs_3(HSO_4)_2(H_2PO_4)$.

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Solid solution studies in the $CsHSO_4$-CsH_2PO_4 system carried out in a search for compounds with unique hydrogen-bonding schemes and related phase transitions, yielded the compound β-$Cs_3(HSO_4)_2(H_2PO_4)$. The compound appears to be a disordered form of α-$Cs_3(HSO_4)_2(H_2PO_4)$ recently reported by this group. The β-form crystallizes in space group C2/c and has lattice parameters a = 20.04(1), b = 7.854(5), c = 8.954(5)Å and $\beta = 100.11(2)°$. In comparison, the a form crystallizes in space group $P2_1/n$ and has the following lattice parameters: a = 19.546(3), b = 7.8798(10), c = 9.1854(17) Å and $\beta = 100.536(14)°$. The arrangement of Cs^+, SO_4^-, and $PO_4^=$ ions are virtually identical in the two forms $Cs_3(HSO_4)_2(H_2PO_4)$: both exhibit "zig-zag" chains of hydrogen-bonded XO_4 groups (where X = 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 a form is almost double that of the latter. In particular, in the