

for intermolecular interactions in the monoclinic paraffins. This value sharply decreases in the region of “rotator” phases existence and equals to zero in H_{rot} . A statistic and dynamic model was proposed, which provides an adequate description of the observed effect [2].

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Keywords: *n*-paraffins, polymorphism, X-ray - FTIR

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Structure and Properties of [4-NH₂C₅H₄NH][BiCl₄]

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The halogenoantimonates(III) and halogenobismuthates(III) of the general formula $R_aM_bX_{3b+a}$ (where R denotes organic cations, X = Cl, Br, I and M = Sb, Bi) form a large group of ferroelectric crystals [1]. The title crystal [4-NH₂C₅H₄NH][BiCl₄] (abbreviation – 4APCB) is closely related to the recently found antimonate(III) analog [4-NH₂C₅H₄NH][SbCl₄] [2], which reveals interesting ferroelectric properties with intermediate incommensurate phases. 4APCB undergoes at 252 K structural phase transition (PT) of first order. The room temperature structure (phase I) is monoclinic, space group Cc with $a = 13.229$, $b = 13.505$, $c = 7.350$ Å and $\beta = 120.31^\circ$. The structure is composed of BiCl₄⁻ ions which form infinite chains through the crystals via chloride linkages. Each bismuth lies in a distorted octahedral environment. The 4-aminopyridinium cation reveals substantial disorder. The low temperature phase (II) is monoclinic, space group P2₁/c with $a = 11.1660(7)$, $b = 13.5857(8)$, $c = 7.2750(4)$ Å and $\beta = 93.777(5)^\circ$. Over the phase II the organic cations are fully ordered. The structural analysis, calorimetric (DSC) and spectroscopic studies (IR) show that the PT is governed by the dynamics of the 4-aminopyridinium cations.

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Keywords: halogenobismuthate(III), disorder, phase transition

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Structure Transformations in the Saturated Hydrides ZrV₂H_{4<x<6}

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We have studied, by means of neutron powder diffraction, the structure transformations caused by hydrogen redistributions in the Laves saturated hydrides ZrV₂H_x, 4<x<6. In the range of 4<x<5, the uncommon order-disorder phase transition has been found [1]. Unlike the known transitions in the unsaturated hydrides, x<4, it results in change of hydrogen surroundings when hydrogen ordering. As a result, the novel hydrogen superstructure ZrV₂H₅, with the atypical hydrogen surroundings, forms [2]. At maximum hydrogen saturation, near x=6, whatever phase transitions are eliminated. The maximum hydride ZrV₂H₆ exists only as ordered, and any attempt to disarrange the hydrogen results in hydrogen discharge down to x=5. The crystal structure of ZrV₂H₆ has been determined [3]. It is advance of the Spinel-type structure found earlier in the saturated hydrides ZrTi₂H₄ and HfTi₂H₄. The work was partly supported by the Russian Foundation for Basic Research and Russian State Program HIII-2037.2003.2.

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50, 356-357.

Keywords: hydrides, neutron powder diffraction, phase transitions and structure

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Structure and Phase Transitions of Some Crystals Containing [(CH₃)₃NH₂]⁺ and MeCl₄

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Results of our investigation of crystal structure and phase transitions of some crystals containing a bivalent metal, chlorine anion, and dimethylammonium (DMA) cations are reported. Studies of the crystals are of great interest, since data of the crystal structure of this compound are very scarce and mechanisms of phase transitions in them are not available. It was established that the crystal were grown from solution with copper chlorides have the composition [(CH₃)₂NH₂]₂CuCl₄[(CH₃)₂NH₂]Cl and, in room temperature are describes by orthorhombic space group *Pna*2₁. The structure of the crystals is built of CuCl₄ tetrahedral, three structure nonequivalent DMA groups, and individual chloride ions, which are links via an extended hydrogen bond system into three-dimensional framework. The unit cell parameters are measure as function of temperature. The crystals undergo jump-wise phase transition into incommensurate modulated phase at 279 K and commensurate modulated phase at 253 K, respectively. The result of our studies demonstrated that the crystals obtained from solution containing cadmium were grown in orthorhombic system [(CH₃)₂NH₂]₅Cd₃Cl₁₁ as well as monoclinic system [(CH₃)₂NH₂]₂CdCl₄. The temperature curves of unit cell parameter and the vicinity of phase transition are reported. At room temperature [(CH₃)₂NH₂]₂CoCl₄ belong to the *P2*₁/*c* space group and have ferroelectric properties in the temperature range 227-260 K. The crystals of this family has complicated system of hydrogen bonds and are a great interest because of ordering of hydrogen bonds and changes in cation dynamics pay an important role in the processes of phase transitions.

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Striking Effect of Pressure and Temperature on PdSe₂ Allotropes

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Under ambient conditions, PdSe₂ adopts the PdS₂-type structure (o-PdSe₂). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and ab initio calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-PdSe₂), strongly related to the o-PdS₂. Using the experimental data obtained at 20°C and 300°C, we examined the order of the PdSe₂ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state.

We also found that the cell volume of c-PdSe₂ was smaller at 300°C than at 20°C by nearly 40%. Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fledgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI₂-type structure. It probed that all MSE₂ (M=transition metal) structures are linked. We evidenced the interconversion path between