

CRYSTAL LATTICE DILATATION IN Cd_{1-x}Cr_xSe SPINELS WITH GALLIUM ADMIXTURESA. Waskowska¹ L. Gerward² J. Staun-Olsen³ E. Malicka⁴¹Institute For Low Temperature And Structure Research, Polish Academy of Sciences WROCLAW 50 422 POLAND²Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark ³N. Bohr Institute, Oersted Laboratory, University of Copenhagen, 2100 Copenhagen, Denmark ⁴Institute of Chemistry, Silesian University in Katowice, 40 007 Katowice, Poland

These compounds crystallize in cubic structure, space group Fd-3m, and show normal cation distribution. Since the magnetic interactions related to the spin ordering in the Cr sublattice depend on interatomic distances, it was interesting to study the behaviour of the chemically modified spinel at non-ambient conditions of temperature and pressure. Single crystals were cooled to about 100 K and the lattice parameters were measured on the Huber 4-circle diffractometer. Well above the Curie temperature, the magnetostriction effect caused a deviation from the Grueneisen-Debye behaviour. The unit cell expanded when the crystal ordered ferromagnetically. For the samples with Ga admixtures small tetragonal and orthorhombic deformations were observed at about 285 K. Simultaneously, the magnetostriction became weaker, indicating that some paths of the direct exchange interactions between the nearest-neighbour Cr ions appeared to be broken. High-pressure studies show that the bulk modulus is about 100 GPa. This is considerably lower than for the oxide-based spinels, where the bulk modulus is about 200 GPa. A structural phase transformation occurs at about 100 GPa.

Keywords: SPINELS NON AMBIENT CONDITIONS**SYNCHROTRON X-RAY POWDER DIFFRACTION STUDY ON SUCCESSIVE PHASE TRANSITIONS IN AZnPO₄ (A:Rb, Cs)**I. Yamashita¹ H. Kawaji¹ T. Atake¹ Y. Kuroiwa² A. Sawada²¹Tokyo Institute of Technology Materials And Structures Laboratory 4259 Nagatsuta-Cho, Midori-Ku YOKOHAMA 226-8503 JAPAN ²Department of Physics, Faculty of Science, Okayama University

The successive phase transitions in AZnPO₄ (A: Rb, Cs) were studied with synchrotron X-ray powder diffraction and DTA, and the detailed mechanism of the transitions was discussed. Single crystals of AZnPO₄ (A: Rb, Cs) were synthesized by a flux method, and ground to fine powder for the diffraction measurements. The diffraction experiments were done with BL02B2 at SPring-8 Japan. The Rietveld and MEM analyses were carried out using RIFN-2000 and MEED. In CsZnPO₄ (CZP) bulk single crystal, I-II, II-III and III-IV phase transitions were observed at 583 K, 533 K and 220 K, respectively. In phase I, positional disorder of oxygen atoms were observed and we concluded that the I-II phase transition should be of order-disorder type. It has been known that the RZP has two phase transitions at 1143 K, 753 K. In the present study, a new phase transition was found as endothermic peak at 490 K by DTA. Thus RZP has four phases above room temperature; we named phase I (highest temperature phase), II, III (newly found phase) and IV (room temperature phase). The Rietveld analysis suggests that the crystal structure of phase II, III in RZP is the same as that of phase II, III in CZP, and they have similar temperature dependence of lattice parameter. We conclude that the phase transition sequence of RZP is similar to that of CZP and the crystal structure of the lowest temperature phase IV in CZP and room temperature phase of RZP may be the same.

Keywords: CsZnPO₄, RbZnPO₄, PHASE TRANSITION**STRUCTURAL PHASE TRANSITION AND DIELECTRIC BEHAVIOR OF o-PHENYLENEBIS(SQUARIC ACID) SALT**S. Yamamura¹ Y. Sugawara¹ H. Terao² T. Sugawara²¹Kitasato University School of Science 1-15-1 Kitasato SAGAMIHARA KANAGAWA 228-8555 JAPAN ²Graduate School of Arts and Sciences, The University of Tokyo

In order to construct a novel hydrogen-bonded system, o-phenylenebis(squaric acid) (o-PBSQ) was synthesized. Phase transitions of its tetramethylammonium (TMA) salt were observed around 300 K and 120 K through temperature dependence of dielectric permittivity. Enthalpy change of the transition around 300 K was estimated to 0.32 kJ/mol based on differential scanning calorimetry (DSC) measurements. Crystal structures of three phases were determined. X-ray diffraction data were collected by a Rigaku MERCURY CCD system. Crystal data are: phase I (at 350 K), tetragonal, $P4_2/n$, $a=14.472(3)$, $c=16.713(4)$ Å, $Z=8$; phase II (at 179 K), monoclinic, $P2_1/n$, $a=14.468(6)$, $b=32.758(14)$, $c=14.391(4)$ Å, $\beta=90.004(15)^\circ$, $Z=16$; phase III (at 112 K), monoclinic, $P2_1$, $a=14.466(6)$, $b=32.499(13)$, $c=14.373(3)$ Å, $\beta=90.034(15)^\circ$, $Z=16$. In all phases, o-PBSQ molecules form a dimer through two O-H...O hydrogen bonds with O...O distances of 2.44 – 2.47 Å. In phase I, the two hydrogen-bonded O atoms are related by the 4_2 screw axis, and hydrogen atoms locate at the center of hydrogen bonds on difference Fourier maps. It is not clear whether the hydrogen atom remains at the center in phase II and III at the present stage. Large librational motion of TMA in phase I was suppressed in phase II and III. Breakdown of symmetry is caused by shifts of o-PBSQ dimers along the short axes of dimers and orientational displacements of TMA. Increment of dielectric permittivity at transition temperatures may be caused by movements of negative (o-PBSQ dimer) and positive (TMA) charges.

Keywords: PHASE TRANSITION, SQUARIC ACID DERIVATIVE, DIELECTRIC PROPERTY**STRUCTURAL PHASE TRANSITIONS IN TETRAMETHYLAMMONIUM HYDROGEN CHALCOGENATES: [N(CH₃)₄]HXO₄ - COMPOUNDS WITH HIGH PROTONIC CONDUCTIVITY**M. A. Zakharov¹ E. V. Kosterina¹ L. A. Aslanov¹ E. Kemnitz² S. I. Troyanov¹¹Moscow State University Chemistry Department Leninskie Gory, MSU, Chemistry Department MOSCOW 119899 RUSSIA ²Institute of Chemistry, Humboldt University, Berlin, 12489, Germany

Alkali metal acid chalcogenates, especially the compounds of the MHXO₄-family are known to show phase transitions to the states with high protonic conductivity. Recently, new members of this family have been discovered - [N(CH₃)₄]HXO₄, X=Se (TMHSe), S (TMHS). TMHS and TMHSe were synthesized and investigated by differential thermal analysis and single crystal X-ray diffraction at room and higher temperatures. TMHSe shows three phase transitions at 354 K (phase III to phase II), 371 K (II to I), and 397 K. Thermal effects of the transitions are 75 J/mol for III-II and 12 kJ/mol for II-I. TMHSe crystals were analyzed at room temperature (III), 363 K (II), and 380 K (I). All three structures consist of isolated tetramethylammonium cations and HSeO₄-tetrahedra connected by H-bonds. Structural differences concern degree of disorder and hydrogen bonding systems (HBS). In III, two HSeO₄-tetrahedra are linked by two H-bonds to cyclic dimers. The similar HBS is in II, but each HSeO₄-group is disordered between two positions. In I, HBS consists of cyclic tetramers of selenate anions, every anion being also disordered between two positions. Preliminary measurements indicated that I possesses high protonic conductivity. Anhydrous TMHS was investigated at room temperature, 378 K, and 445 K. The phases at higher temperatures show a high protonic conductivity, but the structural changes seem to be very small, at least for the non-hydrogen atoms arrangement. TMHS-monohydrate shows the phase transition at 169 K from high temperature cubic form to the rhombohedral one. The HSO₄-anions are highly disordered in both forms, but the degree of H₂O-disordering becomes smaller in low temperature modification.

Keywords: PROTONIC CONDUCTIVITY, PHASE TRANSITIONS, HYDROGEN BONDING