o.m13.p13 New structural members of polysulfide family. N.V. Podberezskaya, N.V. Pervukhina, S.V. Belaya, I.G.Vasilyeva, S.V. Borisov, *Institute of Inorganic Chemistry, Novosibirsk, Russia.*

Keywords: polychalcogenides, crystal chemistry, structure.

We studies of the Ho-S system by structural and equilibrium diagrams methods for identification of individual phases and their stability fields. The crystals were obtained by spontaneous crystallization from KI melt and Ho_2S_3, S components (10.1:1.2:0.54) in sealed quartz ampoules and have a different shape and colour (from red-orange to dark) according to crystal sizes. We have determined the crystal structures and estimated the integer stoichiometric relations for two polysulfide phases (CAD-4 diffractometer by a standard technique, MoK_α- radiation, graphite monochromator). Dark crystal I $HoS_{1.885(5)}$ of the 0.16 mm thickness has the habitus of a square prism with well-marked {101} and {121} faces, and sp.gr. P4/nmm, a=3.820(1), c=7.840(3) Å, V=114.40(6) Å^3, z=2, d_{calc}=6.542g/cm^3, R=0.0520 for 184 $I_{hkl} > 2\sigma_I$ independent reflections. Red-orange crystal II $HoS_{1.863(8)}$ has the shape of a thin rectangular plate (d=0.08 mm) and sp.gr. $P2_1/m$, a=10.961(2), b=11.465(2), c=10.984(2) Å, β=91.27(3)°, V=1380.0(4) Å^3, z=24, d_{calc}=6.486 g/cm^3, R=0,0596 for 5354 $I_{hkl}>2\sigma_I$ independent reflections. In these compounds, the Ho atom is surrounded by 9 S atoms (8+1 for the three atoms in II) to form one-capped square antiprisms. The Ho-S distances, regardless of the S^{2-} or $(S_2)^{2-}$ type, vary in the 2.717 - 3.067 Å range; the maximum distance to the rest atoms is 3.684 Å. The structures belong to the PbFCl type and are compoused of $...(S_2)^{2-}...Ho^{3+}...S^{2-}...S^{2-}...Ho^{3+}...(S_2)^{2-}...$ layer sets which have a different spatial orientation relative to the unit-cell axes. The interlayer $S^{2-}...S^{2-}$ and $S^{2-}...(S_2)^{2-}$ distances are shortened as against the ionic radii sum and vary in the 3.331 -3.558 and 3.029 - 3.784 Å ranges for the first and second types, respectively. There are the calculated values of the occupancy factors and densities for HoS_{2-x} (x=0.25-0) in I and the most probable formulas of the rational compositions in the same x-interval for II.

o.m13.p14 Phase transition and temperature induced switch of Jahn-Teller deformation direction in $Cs_2Cu(ZrF_6)_2$ $6H_2O$. P.E. Tomaszewski, A. Pietraszko and K. Lukaszewicz, *Institute of Low Temperature and Structure Research of PASci., 50-950 Wroclaw, Poland,* M.A. Augustyniak-Jablokow, *Institute of Molecular Physics of PASci., 60-179 Poznan, Poland.*

Keywords: phase transition, negative thermal expansion, Jahn-Teller effect.

The crystal structure of dicaesium copper(II) bishexafluorozirconate hexahydrate, $Cs_2Cu(ZrF_6)_2$ $6H_2O$, has not been so far investigated. We have collected the X-ray diffraction data by using single-crystal KM4-CCD diffractometer (KUMA Diffraction, Wroclaw, Poland) at both, room temperature and 150 K. Both structures were determined in the same space group $P2_1/n$ (No. 14). The determination at low temperature was less accurate due to the twinning. Lattice parameters at room temperature are following: a = 6.929, b = 10.530, c = 11.776 A, β = 92.37°, whereas at 150 K: a = 6.955, b = 10.373, c = 11.974 A, β = 95.31°.

Due to the contraction of c and β parameters the resulting volume thermal expansion is negative which is rather unusual.

We observed, moreover, a considerable change in the geometry of $Cu(H_2O)_6^{2+}$ ion. Interatomic distances at room temperature: Cu-O1 = 2.010, Cu-O2 = 2.094, Cu-O3 = 2.153 A, become at 150 K: 1.992, 2.284 and 2.013 A, respectively, indicating on the switch of the Jahn-Teller deformation direction. A comparison of lattice and atomic parameters at room and low temperature indicates that this switch may occur at about 240 K.

From the temperature dependence of the β angle, which reaches 90° at about 320 K, we could expect the phase transition to the high-temperature phase of orthogonal system (at least orthorhombic symmetry). This phase transition is also observed by DSC measurements. However, the surface dehydration of the sample did not allow to study the high temperature phase.

Both, the change of crystal system and the appearance of the twinning indicate on the ferroelastic character of title crystal below 320 K.