PS08.01.25 CRYSTAL STRUCTURE OF HgMoO4, HgV2O5, Hg2V2O7, AND Hg2As2O6. Manfred H. Möller, Annemarie L. Wessels, Wolfgang Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany.

The title compounds were prepared by reactions of binary and ternary oxides in evacuated silica tubes at temperatures between 400 and 550°C. Their crystal structures were determined and refined from single-crystal X-ray diffractometer data. HgMoO4: P21/c, a = 913.9(1) pm, b = 551.3(1) pm, c = 1429.1(2) pm, Z = 2, R = 0.043 (129 structure factors, 66 variable parameters). HgV2O5: P1, a = 359.2(1) pm, b = 475.2(1) pm, c = 858.8(1) pm, α = 88.32(1), β = 79.60(1), γ = 89.30(1), Z = 2, R = 0.034 (1763 F2, 32 v). Hg2V2O7: P21/n, a = 367.3(1) pm, b = 1650.3(1) pm, c = 1425.5(1) pm, β = 89.99(1). Z = 8, R = 0.038 (1666 F, 32 v). Hg2As2O6: R3c, a = 1665.3(1) pm, c = 1083.79(7) pm, Z = 6, R = 0.037 (1661 F, 62 v).

HgMoO4, HgV2O5, and Hg2V2O7 are (HgI) compounds with mixed-valent Hg(II) compounds with isolated Hg atoms. In HgAs2O6, the mercury atoms form almost equilateral Hg3 triangles. These coordination polyhedra share corners and edges, thus forming two-dimensionally infinite sheets. The vanadium atoms are irregularly surrounded by five oxygen atoms. These coordination polyhedra share edges, thus forming infinite (V03I)n chains, which are aligned parallel to each other. The tetrahedral AsO4 groups are linked only via Hg triangles. Thus, the central atoms of the unions are in their highest oxidation state and the compounds may be represented by the formulas (Hg22+)(MoO4)2(MoO4)2(Hg22+)(V03I)·(Hg22+·MoO4)·(V03I)·(Hg22+·HgV04·Hg22+·MoO4)

PS08.01.26 CRYSTAL STRUCTURE OF MIXED-VALENCE CoV08 WITH UNUSUAL METAL DISTRIBUTION. Yoshiho Okai, Takeshi Yao, and Naohi Yamamoto, Faculty of Integrated Human Studies, Faculty of Engineering, Kyoto University, Kyoto 606 Japan.

In the CoO-V2O5-V2O3 system studied at 600°C only CoO3+ is found as a V(V) mixed-valence compound. It was originally formulated as CoO(V2O5)2(O.90sE5) with two polymorphs α and β phases. α phase transforms reversibly into β phase at 650 ±8°C. It was reported that a phase crystallizes in the body-centered orthorhombic system but the structure has remained unknown. In the present study single crystals of α-CoV2O5 were grown in the hydrothermal Co-O-V-OH2 system. It crystallizes in the orthorhombic system Ibm with a =14.2928(6)Å, b=9.8906(6)Å, c =8,3950(8)Å and Z=8. The structure was refined to R(refl)=0.034/0.035 for 1558 reflections with 0≤3(θ). There are three kinds of metal sites, namely octahedral M (16k) for Mn, Co, V (1), tetrahedral V (2) (4j) and trigonal-bipyramidal V (3) (8j) where M site is occupied by Co and V atoms evenly. The framework structure is constructed as that zigzag chains of edge-shared MO6 octahedra running along the c-axis are linked by sharing O(5) atoms along the b-axis forming slabs of MO6 octahedral parallel to the b-plane and the slabs are joined by VO4 tetrahedra and VO4 trigonal bipyramids. The valence states of metal sites were estimated as Co3+ and V4+ for M and V5+ for V (2) and V (3). It is noteworthy that the metal distribution over M site is not random but restricted to Co-O(5)-V in neighboring MO6 through O(5) vertex, which accounts for the even occupancies of Co and V atoms in M site and further ensures the stoichiometric composition CoV08.

The magnetic susceptibility curve exhibits a sharp peak at 8K suggesting the onset of antiferromagnetic order and the value of effective moment is well corresponding to the formula (Co3+V4++V5+)2 V5+O4.


PS08.01.27 STRUCTURE OF HIGHTEMPERATURE PHASES OF THALLIUM NITRATE. P. U. M. Sastry, A. Sequeira, Solid State Physics Division, B.A.R.C., Mumbai 400085, India.

TNO exhibits structural transitions from orthorhombic phase (III) at R. T. to hexagonal phase (II) (T=79°C) and then to cubic phase (I) (T=147°C). These transitions are believed to be associated with reorientation of planar nitrate ions. The structure of phase III is reported in an earlier single crystal neutron study. In the present work, the structures of phase II (115°C) and phase I (170°C) are determined using powder neutron diffraction. Refinements using Rietveld technique indicate that the structures of phase II (Sp.Gr. P21/c; α=7.451(1)Å, Z=6) and phase I (Sp.Gr. Pm3m; α=307(1)Å,Z=6) are similar to those of RbNO3 (IV) and Rb2O3 (III) respectively. The final R-values (Rp) for phases II and I are 3.8% and 5.1%. In all the three phases, nitrate ions are oriented perpendicular to the three edges of surrounding Ti-cubes with equal proportions in phases II and I. Transformation to phase II from phase III involves an out-of-plane flip of 90° for one of the eight nitrate ions in the cell. While the nitrate ions are ordered in phases III and II, they exhibit a 12-fold orientational disorder in phase I with one of the N=0 bonds oriented parallel to an edge of Ti-cube. Refinements rule out the earlier models proposed in literature for phases II and I in which the nitrate ions are oriented normal to the diagonal of Ti-cube.


PS08.01.28 THE STRUCTURE OF La25(BO3)027. E. Schweda, K. Wurst, J. H. Lin, M. Z. Su, Institut für Anorganische Chemie, Universität Tübingen, Germany, Inst. für Allg. und Anorg. Chemie, Universität Innsbruck, Austria, Dept. of Materials Chemistry, Feketo University, Beijing 100871, China.

Previously La25(BO3)027 was described as La3BO6 with the remark that the samples contain a small amount of unreacted oxide. Very small colourless crystals of La25(BO3)027 were grown from La2O3 and H3BO3. La25(BO3)027 crystallizes in the monoclinic space group P21/c with the lattice constants a = 692.0(1) pm, b = 1292.3(1) pm, c = 1457.1(1) pm and β = 99.41(1)°. A close inspection of this structure reveals a certain relationship to the (CaF2) fluorite structure, both from the structure and the composition point of view. At a first sight, neglecting the boron atoms in the structure, the composition will be close to "La2O7" (La2O32.83). Furthermore the structure of La25(BO3)027 can be considered as a distorted version of the fluorite structure. To emphasize this feature one of the "fluorite" layers with a stacking sequence O-La-O is presented in fig. 1. The sheets are oriented perpendicular to the [101] lattice direction.

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References