

PS08.01.25 CRYSTAL STRUCTURES OF $\text{Hg}_2\text{Mo}_5\text{O}_{16}$, HgVO_3 , Hg_2VO_4 , AND $\text{Hg}_9\text{As}_4\text{O}_{16}$. 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. $\text{Hg}_2\text{Mo}_5\text{O}_{16}$: $P2_1/c$, $a = 913.9(1)$ pm, $b = 551.3(1)$ pm, $c = 1429.1(2)$ pm, $\beta = 110.65(1)^\circ$, $Z = 2$, $R = 0.043$ (1129 structure factors, 66 variable parameters). HgVO_3 : $P1$, $a = 359.2(1)$ pm, $b = 475.2(1)$ pm, $c = 858.8(1)$ pm, $\alpha = 88.32(1)^\circ$, $\beta = 79.60(1)^\circ$, $\gamma = 89.30(1)^\circ$, $Z = 2$, $R = 0.034$ (1763 F, 32 v). Hg_2VO_4 : $P2_1/n$, $a = 367.3(1)$ pm, $b = 1650.3(1)$ pm, $c = 1425.5(1)$ pm, $\beta = 89.99(1)^\circ$, $Z = 8$, $R = 0.038$ (1668 F, 91 v). $\text{Hg}_9\text{As}_4\text{O}_{16}$: $R3c$, $a = 1665.3(1)$ pm, $c = 1083.79(7)$ pm, $Z = 6$, $R = 0.037$ (1661 F, 62v).

$\text{Hg}_2\text{Mo}_5\text{O}_{16}$ and HgVO_3 are Hg(I) compounds with Hg_2 pairs, Hg_2VO_4 is a mixed valent Hg(I, II) compound with Hg_2 pairs and isolated Hg atoms. In $\text{Hg}_9\text{As}_4\text{O}_{16}$ the mercury atoms form almost equilateral Hg_3 groups with the oxidation number +4. The molybdenum atoms have distorted octahedral coordination. These MoO_6 octahedra 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 $(\text{VO}_3^{1-})_n$ chains, which are aligned parallel to each other. The tetrahedral AsO_4 groups are linked only via Hg_3 triangles. Thus, the central atoms of the anions are in their highest oxidation state and the compounds may be represented by the formulas $(\text{Hg}_2^{2+})_n(\text{MO}_5\text{O}_{16}^{2-})_n$, $(\text{Hg}_2^{2+})_n(\text{VO}_3^{1-})_{2n}$, $(\text{Hg}_2^{2+} \cdot 2\text{HgO})_n(\text{VO}_3^{1-})_{2n}$, and $(\text{Hg}_3^{4+})_3(\text{AsO}_4^{3-})_4$.

PS08.01.26 CRYSTAL STRUCTURE OF MIXED-VALENCE α - CoV_3O_8 WITH UNUSUAL METAL DISTRIBUTION. Yoshio Oka¹, Takeshi Yao² and Naoichi Yamamoto¹, Faculty of Integrated Human Studies¹, Faculty of Engineering², Kyoto University, Kyoto 606 Japan

In the $\text{CoO-V}_2\text{O}_5$ system studied at 600°C only CoV_3O_8 is found as a V(IV,V) mixed-valence compound¹. It was originally formulated as $\text{Co}_{1+y}(\text{V}_3\text{O}_8)_2$ ($0.90 \leq y \leq 1$) with two polymorphs α and β phases; α phase transforms reversibly into β phase at $650 \pm 8^\circ\text{C}$. 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 - CoV_3O_8 were grown in the hydrothermal $\text{CoI}_2\text{-VO(OH)}_2$ system. It crystallizes in the orthorhombic system $Ibam$ with $a = 14.3298(6)\text{Å}$, $b = 9.8906(6)\text{Å}$, $c = 8.3950(8)\text{Å}$ and $Z = 8$. The structure was refined to $R/R_w = 0.034/0.030$ for 1558 reflections with $I > 3\sigma(I)$. There are three kinds of metal sites, namely octahedral M (16k) for $M = \text{Co}$, V(1), tetrahedral V(2) (8j) 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 MO_6 octahedra running along the c -axis are linked by sharing O(5) atoms along the b -axis forming slabs of MO_6 octahedra parallel to the bc -plane and the slabs are joined by VO_4 tetrahedra and VO_5 trigonal bipyramids. The valence states of metal sites were estimated as Co^{2+} and V^{4+} for M and V^{5+} 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 MO_6 through O(5) vertex, which accounts for the even occupancies of Co and V atoms in M site and further ensures the stoichiometric composition CoV_3O_8 . 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 $(\text{Co}^{2+}_{0.5}\text{V}^{4+}_{0.5})_2\text{V}^{5+}_2\text{O}_8$.

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

TlNO_3 exhibits structural transitions from orthorhombic phase (III) at R. T. to hexagonal phase (II) ($T_c = 79^\circ\text{C}$) and then to cubic phase (I) ($T_c = 147^\circ\text{C}$). 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 study¹. In the present work, the structures of phase II (at 115°C) and phase I (at 170°C) are determined using powder neutron diffraction. Refinements using Rietveld technique indicate that the structures of phase II (Sp.Gr. $P3_1$; $a = 10.435(1)\text{Å}$, $c = 7.451(1)\text{Å}$, $Z = 9$) and phase I (Sp.Gr. $Pm3m$, $a = 4.307(1)\text{Å}$, $Z = 1$) are similar to those of RbNO_3 (IV) and RbNO_3 (III) respectively. The final R -values (R_p) 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 Tl-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-O bonds oriented parallel to an edge of Tl-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 Tl-cube.

1. P. U. M. Sastry, H. Rajagopal and A. Sequeira, Acta Cryst., C50, 1854 (1994).

PS08.01.28 THE STRUCTURE OF $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$. E. Schweda,^a K. Wurst,^b J.H. Lin,^c M.Z. Su^a Institut für Anorganische Chemie, Universität Tübingen, Germany^b Inst. für Allg. und Anorg. Chemie, Universität Innsbruck, Austria^c Dept. of Materials Chemistry, Peking University, Beijing 100871, China

Previously $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ was described as La_3BO_6 with the remark that the samples contain a small amount of unreacted oxide [1]. Very small colourless crystals of $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ were grown from La_2O_3 and H_3BO_3 . $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ crystallizes in the monoclinic space group $P2_1/c$ with the lattice constants $a = 692.0(1)$ pm, $b = 1292.3(1)$ pm, $c = 1457.1(1)$ pm and $\beta = 99.41(1)^\circ$.

A close inspection of this structure reveals a certain relationship to the (CaF_2) 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 " LaO_2 " ($\text{La}_{26}\text{O}_{52-x}\text{B}_8$). Furthermore the structure of $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$ 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

1. Gmelin Handbook RE Main Vol.C 11b, p.390

