

**PS08.01.25 CRYSTAL STRUCTURES OF  $\text{Hg}_2\text{Mo}_5\text{O}_{16}$ ,  $\text{HgVO}_3$ ,  $\text{Hg}_2\text{VO}_4$ , 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).  $\text{HgVO}_3$ :  $P1$ ,  $a = 359.2(1)$  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).  $\text{Hg}_2\text{VO}_4$ :  $P2_1/n$ ,  $a = 367.3(1)$  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  $\text{HgVO}_3$  are  $\text{Hg(I)}$  compounds with  $\text{Hg}_2$  pairs,  $\text{Hg}_2\text{VO}_4$  is a mixed valent  $\text{Hg(I, II)}$  compound with  $\text{Hg}_2$  pairs and isolated Hg atoms. In  $\text{Hg}_9\text{As}_4\text{O}_{16}$  the mercury atoms form almost equilateral  $\text{Hg}_3$  groups with the oxidation number +4. The molybdenum atoms have distorted octahedral coordination. These  $\text{MoO}_6$  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  $\text{AsO}_4$  groups are linked only via  $\text{Hg}_3$  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  $\alpha$ - $\text{CoV}_3\text{O}_8$  WITH UNUSUAL METAL DISTRIBUTION.** Yoshio Oka<sup>1</sup>, Takeshi Yao<sup>2</sup> and Naoichi Yamamoto<sup>1</sup>, Faculty of Integrated Human Studies<sup>1</sup>, Faculty of Engineering<sup>2</sup>, Kyoto University, Kyoto 606 Japan

In the  $\text{CoO-VO}_2\text{-V}_2\text{O}_5$  system studied at 600°C only  $\text{CoV}_3\text{O}_8$  is found as a  $\text{V(IV,V)}$  mixed-valence compound<sup>1</sup>. 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  $\alpha$  and  $\beta$  phases;  $\alpha$  phase transforms reversibly into  $\beta$  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  $\alpha$ - $\text{CoV}_3\text{O}_8$  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  $\text{MO}_6$  octahedra running along the  $c$ -axis are linked by sharing O(5) atoms along the  $b$ -axis forming slabs of  $\text{MO}_6$  octahedra parallel to the  $bc$ -plane and the slabs are joined by  $\text{VO}_4$  tetrahedra and  $\text{VO}_5$  trigonal bipyramids. The valence states of metal sites were estimated as  $\text{Co}^{2+}$  and  $\text{V}^{4+}$  for M and  $\text{V}^{5+}$  for V(2) and V(3). It is noteworthy that the metal distribution over M site is not random but restricted to  $\text{Co-O(5)-V}$  in neighboring  $\text{MO}_6$  through O(5) vertex, which accounts for the even occupancies of Co and V atoms in M site and further ensures the stoichiometric composition  $\text{CoV}_3\text{O}_8$ . 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  $(\text{Co}^{2+}_{0.5}\text{V}^{4+}_{0.5})_2\text{V}^{5+}_2\text{O}_8$ .

1) A. Cassalot and P. Hagenmuller, J. inorg. nucl. Chem., 31, 3049 (1969).

**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

$\text{TlNO}_3$  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 study<sup>1</sup>. In the present work, the structures of phase II (at  $115^\circ\text{C}$ ) and phase I (at  $170^\circ\text{C}$ ) 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  $\text{RbNO}_3$  (IV) and  $\text{RbNO}_3$  (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  $90^\circ$  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,<sup>a</sup> K. Wurst, <sup>b</sup>J.H. Lin, <sup>c</sup>M.Z. Su <sup>a</sup>Institut für Anorganische Chemie, Universität Tübingen, Germany <sup>b</sup>Inst. für Allg. und Anorg. Chemie, Universität Innsbruck, Austria <sup>c</sup>Dept. of Materials Chemistry, Peking University, Beijing 100871, China

Previously  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  was described as  $\text{La}_3\text{BO}_6$  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  $\text{La}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ .  $\text{La}_{26}(\text{BO}_3)_8\text{O}_{27}$  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  $(\text{CaF}_2)$  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<sub>2</sub>" ( $\text{La}_{26}\text{O}_{52-x}\text{B}_8$ ). 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

