CRYSTAL STRUCTURES OF Hg$_2$MO$_4$O$_8$, HgVO$_4$, Hg$_5$VO$_6$ AND Hg$_3$As$_4$O$_{16}$. Manfred H. Möller, Annemarie L. Wessels, Wolfgang Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-KlemmStr. 8, D-48149 Münster, Germany

The title compounds were prepared by reactions of binary and tertiary 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. Hg$_2$MO$_4$O$_8$: P2/c, a = 913.9(1) pm, b = 531.3(1) pm, c = 1249.1(2) pm, $\beta$ = 110.65(1)$^\circ$, $\rho$ = 2, $R$ = 0.043 (1129 structure factors, 66 variable parameters). HgVO$_4$: 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)$^\circ$, $\gamma$ = 93.80(1)$^\circ$, $\rho$ = 2, $R$ = 0.034 (1763 F, 32 V), HgVO$_3$: P2$_1$/n, a = 367.3(1) pm, b = 1650.3(1) pm, c = 1425.5(1) pm, $\beta$ = 89.99(1)$^\circ$, $\rho$ = 8, $R$ = 0.038 (1666 F, 91 V). Hg$_5$As$_4$O$_{16}$: R3c, $\rho$ = 1083.79(7) pm, c = 1884.3(4) pm, $\rho$ = 8, $R$ = 0.037 (1661 F, 62V).

Hg$_2$MO$_4$O$_8$, HgVO$_4$ and Hg$_3$As$_4$O$_{16}$ are Hg(II) compounds with Hg$_2$ pairs, Hg$_5$VO$_6$ is a mixed valent Hg(II) compound with Hg$_2$ pairs and isolated Hg atoms. In Hg$_2$As$_4$O$_{16}$, the mercury atoms form almost equivalent Hg$_2$ groups within the oxidation number +1. The molybdenum atoms have distorted octahedral coordination. These MO$_6$ 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 (VO$_3$)$_n$ chains, which are aligned parallel to each other. The tetrahedral As$_4$O$_{12}$ groups are linked only via Hg triangles. Thus, the central atoms of the anions in their highest oxidation state and the compounds may be represented by the formulas (Hg$_2$)$_3$(MoO$_6$)$_2$As$_4$(H$_2$O)$_3$. (Hg$_2$)$_3$ + 2HgO(VO$_3$)$_2$_2, and (Hg$_2$)$_3$As$_4$(VO$_3$)$_2$.

PS08.01.25 CRYSTAL STRUCTURE OF MIXED-VALENCE $\alpha$-CoVO$_4$ WITH UNUSUAL METAL DISTRIBUTION. Yoshio Okai, Takeshi Yao2 and Naohi Yamamoto, Faculty of Integrated Human Studies, Faculty of Engineering2, Kyoto University, Kyoto 606 Japan

In the Co-O-V$_2$O$_5$ system studied at 600°C only CoVO$_4$ is found as a V(V) mixed-valence compound. It was originally formulated as Co$_{1+y}$(V$_{y}$O$_{5+y}$)O$_2$ (0.90<y<1) with two polymorphs $\alpha$ and $\beta$ phases: $\alpha$: phase transforms reversibly into $\beta$ 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 $\alpha$-CoVO$_4$ were grown in the hydrothermal Co$_3$V$_2$O$_9$O$_2$$_2$ system. It crystallizes in the orthorhombic system Ibam with $a = 14.3298(6)$ Å, $b = 9.8906(6)$ Å, $c = 8.3950(8)$ Å and $\rho$ = 8. The structure was refined to $R_{w}$=0.034/0.030 for 1558 reflections with $\rho$=30T. There are three metal sites, namely octahedral M (16k) for $\alpha$-CoO, V(1), tetrahedral V(2) (8j) and trigonal-bipiramidal 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 be-plane and the slabs are joined by VO$_4$ tetrahedra and VO$_2$ trigonal bipyramids. The valence states of metal sites were estimated as Co$^{2+}$ and V$^{4+}$ for M and V$^{3+}$ for V(2) and V(3). It is noteworthy that the metal distribution over M site is not random but restricted to Co(5j)-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$_2$O$_4$. 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 (Co$^{2+}$V$^{4+}$)$_2$V$^{3+}$O$_4$.  

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

TINO$_2$ exhibits structural transitions from orthorhombic phase III at R. T. to hexagonal phase (II) ($T_c$=89°C) and then to cubic phase (I) ($T_c$=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 (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. P2$_1$1/a, $c=7.451(1)$ Å, $Z=8$) and phase I (Sp.Gr. Pm3m, $a=3.071(1)$ Å, $Z=4$) are similar to those of RbNO$_3$ (IV) and RbBO$_3$(II) 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 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 NO$_3$ 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 La$_2$B$_2$(BO$_3$)$_9$O$_7$, E. Schweda, a K. Wurst, b J. H. Lin, c M. Z. Su Institute für Anorganische Chemie, Universität Tübingen, Germany, Institute für Allg. und Anorg. Chemie, Universität Innsbruck, Austria, -Dept. of Materials Chemistry, Fekeng University, Beijing 100087, China

Previously La$_2$B$_2$(BO$_3$)$_9$O$_7$ was described as La$_2$B$_2$O$_7$ with the remark that the samples contain a small amount of unreacted oxide [1]. Very small colourless crystals of La$_2$B$_2$(BO$_3$)$_9$O$_7$ were grown from La$_2$O$_3$ and H$_3$BO$_3$. La$_2$B$_2$(BO$_3$)$_9$O$_7$ 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$_2$) fluoride 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 "La$_2$O$_7$" (La$_2$O$_7$B$_2$). Furthermore the structure of La$_2$B$_2$(BO$_3$)$_9$O$_7$ can be considered as a distorted version of the fluoride 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
