Electrochemical–hydrothermal synthesis and structure determination of a novel layered mixed-valence oxide: $BaV_7O_{16}\cdot nH_2O$

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The electrochemical–hydrothermal synthesis of a new mixed-valence oxide $BaV_7O_{16}\cdot nH_2O$ ($n \approx 4.4$) with $[V_7O_{16}]$ layers containing both vanadium oxygen tetrahedra and distorted octahedra is reported.

Vanadium oxide bronzes have been the focus of many studies because of their complex structural, physical and chemical properties. Compounds formed by high temperature synthesis and by intercalation reactions of V_2O_5 have been reported.[1–3] Most recently, hydrothermal methods have been shown to be an effective approach for the synthesis of new layered vanadium oxide bronzes containing either inorganic or organic interlayer cations.[3–12] Such materials have been of interest because of their potential application as cathode materials in secondary lithium batteries.[12] The structures of the vanadium bronzes are based on distorted vanadium–oxygen octahedra or square pyramids and VO_4 tetrahedra. The layered structures contain either single layers of corner and edge-shared polyhedra[3–8] or double layers that also contain face-shared units.[9–12] Examples of single layer structures recently reported are $(C_3N_2H_{12})_{0.5}V_2O_5$[3] and $(C_6H_{14}N_2)V_6O_{14}\cdot H_2O$[5,6] while the compounds δ-$M_{0.25}V_2O_5\cdot H_2O$ (M = Ni, Ca)[10] and $NMe_4V_8O_{20}$[12] have double layers.

Hydrothermal reactions can lead to high yields of well developed single crystal products but are known to be very sensitive to the specific reaction conditions used. For example, the pH has been shown to play a critical role in determining the final products of hydrothermal synthesis of vanadium oxides in reactions containing tetramethylammonium cations.[13] At present, we are investigating whether a modification of conventional hydrothermal synthesis in which one of the metal ion reactants is electrochemically introduced can provide better control over product formation. Previous studies of the hydrothermal electrosynthesis of thin films of $BaTiO_3$ and $SrTiO_3$ have been reported but the technique has not been used specifically for the synthesis of new compounds.[14] Here, we report the synthesis and structure of the new layered vanadium oxide bronze $BaV_7O_{16}\cdot nH_2O$ using the electrochemical–hydrothermal method. Other barium vanadium oxide bronzes have been synthesized hydrothermally.[15–17]

The synthesis experiments were performed using a Teflon-lined autoclave fitted with feedthroughs for electrical connections between the electrodes inside the reaction chamber and the external circuit. In a typical experiment, 40 ml of 0.01 M $Ba(NO_3)_2$ solution (pH = 1.2) was sealed in the autoclave. The anode (working electrode) was a vanadium metal plate (20 × 10 × 0.254 mm). A gold foil was used as cathode (counter electrode) and a Pt wire as a pseudo-reference electrode. The experiment was conducted with current densities in the range 0.1–1 mA generated by a commercial power source (MacPile, Biologic Scientific Instruments) at 170 ± 2 °C for 100 h. Black shiny plates of $BaV_7O_{16}\cdot nH_2O$ coprecipitated together with black needles of the known compound BaV_3O_8[15] and an unidentified minor phase.

The tetragonal structure of $BaV_7O_{16}\cdot nH_2O$ is a new structure type in which $[V_7O_{16}]$ double layers are stacked along the [001] unit cell direction with Ba^{2+} ions and H_2O molecules located between the layers (Figs. 1 and 2).‡ There are three different vanadium atom positions in the layers. V(1) and V(2) atoms are coordinated by oxygen atoms to form distorted octahedra while V(3) has tetrahedral coordination. The $V(2)O_6$ distorted octahedra share *trans* edges with two $V(1)O_6$ units to form trimers which in turn are connected by edge sharing $V(1)O_6$ octahedra to form zigzag chains. The chains are interconnected into single layers by sharing one oxygen atom. The layers are stacked along [001] with all of the short V=O oxygen atoms on the same side of the layer. The two octahedral layers are directly connected by sharing common edges to form a double layer of composition $[V_7O_{16}]$. The tetrahedra are located between the distinctive 1 × 2 windows of both octahedral layers.

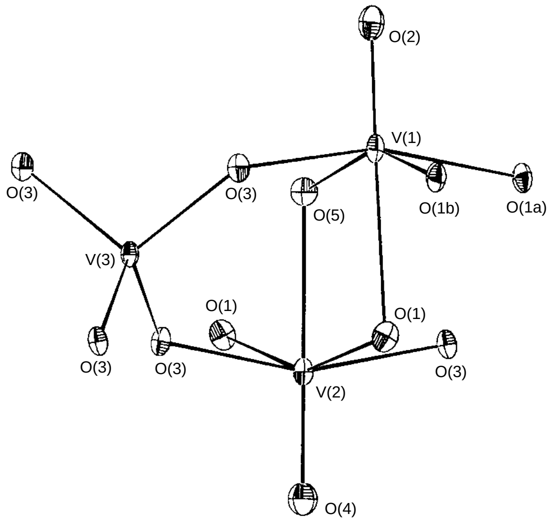

Fig. 1 Coordination environments of the vanadium atoms. Thermal ellipsoids are drawn with 50% probability. Bond lengths (Å): V(1)–O(2) 1.600(5); V(1)–O(5) 1.843(2), V(1)–O(1a) 1.941(4), V(1)–O(1b) 2.006(4), V(1)–O(3) 2.020(4), V(1)–O(1) 2.390(4), V(2)–O(4) 1.611(7), V(2)–O(1) (×2) 1.976(4), V(2)–O(3) (×2) 1.995(4), V(2)–O(5) 2.273(6), V(3)–O(3) (×4), 1.790(4).

The $V(1)O_6$ and $V(2)O_6$ octahedra show distortions typical of V_2O_5 related oxides. The vanadium atoms are displaced from the center of each octahedron along a local [001] direction to give short 'vanadyl' distances of 1.600 and 1.611 Å for V(1) and V(2), respectively. The corresponding distances *trans* to the vanadyl oxygen atoms are 2.390 and 2.273 Å. The $V(1)O_6$ $V(2)O_6$ octahedra are comparably distorted with O···O distances in the range 2.57–2.95 Å [V(1)] and 2.58–2.91 Å [V(2)]. The $V(2)O_6$ octahedron is noticeably elongated in the basal plane along the axis of the trimeric edge-shared unit (2.91 *cf.* 2.58 Å). Bond valence sums were calculated using the parameters for V^{IV}–O.[18] The values calculated are 4.42, 4.18 and 3.94 v.u. for V(1), V(2) and V(3) respectively and are consistent with mixed valence vanadium ions with an average oxidation state of 4.29. The bond valence sums suggest that V(3) which is tetrahedrally coordinated by oxygen atoms [*d*(V–O) = 1.790 Å] is tetravalent. This unusual V^{IV}–O coordination is found only in rare cases such as in the structure of Ba_2VO_4 [average *d*(V–O) = 1.76 Å].[19] The V(1) and V(2) positions are occupied both

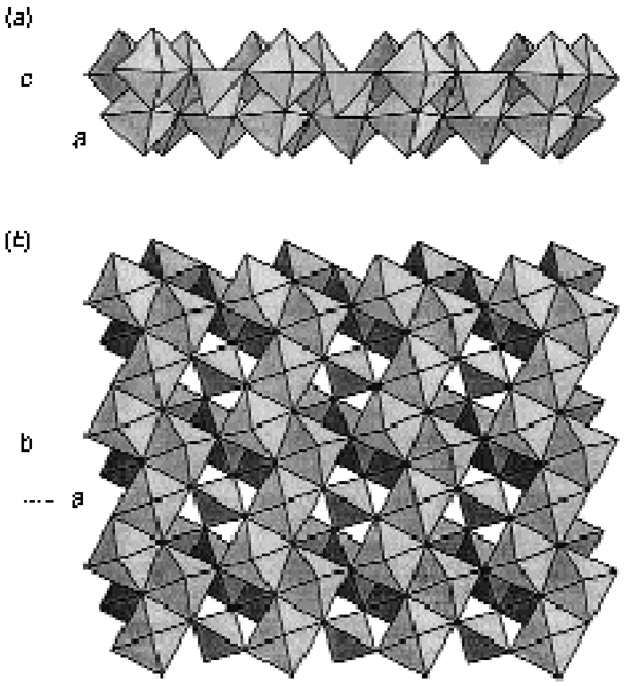

Fig. 2 Projections of the [V_7O_{16}] layer along (*a*) [010] and (*b*) along [001]

by V^{IV} and V^{V}, with some preference for V^{V} at the V(1) position where symmetry is lower.

The barium cations occupy two different interlayer positions both with an occupancy of about one third. The two Ba positions are only 2.61 Å apart and cannot be occupied simultaneously. Both barium atoms are coordinated by vanadyl oxygen atoms from the layers above and below and by interlayer H_2O molecules. One water molecule is located between the Ba cation layer and the vanadate layer and is well ordered. The water molecules located in the same layer as the barium cations are highly disordered. Four distinct partially occupied sites were located and refined to give a total water content $n \approx 4.4$ in $BaV_7O_{16}\cdot nH_2O$. Refinement of the barium occupancies gave a Ba : V atomic ratio of 1.04(1) : 7, in good agreement with a ratio of 0.98 : 7 determined by electron microprobe analysis.§

The structure of the $BaV_7O_{16}\cdot nH_2O$ layers is an example of a new layer topology but is related to other double layer vanadate structures, for example, δ-$Ca_{0.25}V_2O_5\cdot H_2O$[10] and σ-$Zn_{0.25}V_2O_5\cdot H_2O$.[11] In the δ phase, all of the vanadium atoms have distorted octahedral environments. In the layer structure of the σ phase the vanadium atoms are found in distorted octahedral, square pyramidal and tetrahedral coordinations. One of the oxygen atoms in the tetrahedron is not coordinated to other vanadium atoms in the layer, an arrangement observed in several single layer structures.[3–6] In contrast, in the title compound all oxygen atoms in the $V(3)O_4$ tetrahedra are shared with V(1) and V(2) atoms.

In summary, a new layered mixed-valence barium vanadium oxide $BaV_7O_{16}\cdot nH_2O$ with vanadium ions present in both distorted octahedral and tetrahedral coordination environments was synthesized by electrochemical–hydrothermal synthesis. This result together with preliminary data on other vanadium systems suggest that the combination of electrocrystallization under hydrothermal conditions is a generally useful synthetic method.

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Notes and References

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‡ *Crystal data* for $BaV_7O_{16}\cdot nH_2O$, M = 829.1, space group $P4_2/m$, a = 6.1598(4), c = 21.522(2) Å, Z = 4, D_c = 3.38 g cm^{-3}, black thin plate, crystal size 0.15 × 0.15 × 0.01 mm, Mo-Kα radiation (λ = 0.71073 Å), μ = 6.30 mm^{-1}, $2\theta_{max}$ = 57°, $R(F)$ = 0.0517, $wR(F^2)$ = 0.112, GOF = 1.245 for 89 parameters and 819 unique reflections with $I > 2\sigma(I)$.

Intensities were measured on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite-monochromatized Mo-Kα radiation at −50 °C. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s per frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction applied on the intensities was *ca.* 1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Final cell constants were refined using 2547 reflections having $I > 10\sigma(I)$. An absorption correction was first made using the program SADABS based on equivalent reflections. The structure was solved with direct methods and refined using SHELXTL. All atom positions except the disordered water oxygen atoms were derived by direct methods and refined anisotropically in the final refinements. The disordered water oxygen atoms were located from difference maps and refined isotropically with the same thermal parameter and free occupancies. CCDC 182/816.

§ Electron microprobe analysis was carried out with a JEOL JXA-8600 instrument operating at 15 keV with a 10 μm beam diameter and a beam current of 30 nA. Counting times in the range of 40–100 s were used for both peaks and background.

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