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Lone-Pair Self-Containment in Tellurite Tubes: Hydrothermal Syntheses and Structures of $BaTe_3O_7$ and $BaTe_4O_9$

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Traditionally, mixed-metal oxides containing a dense packing of atoms have been prepared in powder (microcrystalline) form by high-temperature ceramic methods.[1] It has recently been shown[2,3] that hydrothermal (or nonaqueous solvothermal) synthesis is a highly effective route to single crystals of new, condensed, anhydrous tellurites. Crystal structures containing Te^{IV} are of interest[4] because of the unpredictable coordination behavior shown by this species due to its stereochemically active lone pair of electrons. In fact, the entire structure is affected by the requirement for "empty" space to accommodate the tellurium lone-pair electrons.[5,6] In this way in particular, they may assist in understanding the properties of technologically important tellurite glasses by rationalizing the connectivity patterns for the Te/O units and the coordination requirements of network-modifying cations.[7,8] Here, we report the mild-condition hydrothermal syntheses and single-crystal structures of two new barium tellurites, $BaTe_3O_7$ and $BeTe_4O_9$. These related phases contain novel, infinite, tellurite tubes and may be regarded as two members of the family of phases denoted $BaTe_nO_{2n+1}$ with $n = 3$ and 4. A ceramic synthesis for $BaTe_4O_9$ was reported some time ago,[9] but no crystallographic details were elucidated.

$BaTe_3O_7$ was prepared from $Ba(OH)_2{\cdot}8H_2O$ (0.318 g, 1 mmol), TeO_2 (0.638 g, 4 mmol), and 10 mL of H_2O, which were placed in a 18-mL capacity Teflon-lined steel bomb. Dropwise addition of concentrated HNO_3 lowered the starting pH from 12 to ~10 and the resulting mixture was heated to 180 °C for 5 days. After removal from the oven and cooling over a few hours, the bomb was opened and the solid product, consisting of 0.62 g of transparent rods (yield based on Ba = 98%), was recovered by vacuum filtration and washing with water and acetone. Reactions carried out at pH 12 (no HNO_3 in the reaction) led to as-yet unidentified powder products.

Single crystals of $BaTe_4O_9$ were prepared from a mixture of $BaCO_3$ (0.199 g, 1 mmol), TeO_2 (0.477 g, 3 mmol), $CoCl_2{\cdot}6H_2O$ (0.238 g, 1 mmol), and 10 mL of H_2O. The starting pH was adjusted to ~10 by the addition of 1 M LiOH solution and the sealed mixture was heated to 180 °C for 3 days. Product recovery as above led to a mixture of pinkish-purple powder, probably $Co(OH)_2$, and a few transparent rods and bars of $BaTe_4O_9$. We have not yet managed to prepare $BaTe_4O_9$ in high yield by hydrothermal methods. Similar syntheses carried out in the absence of cobalt chloride, which possibly controls the pH of the reaction, led only to recrystallized TeO_2. Pure polycrystalline $BaTe_4O_9$ can be made by ceramic methods: a stoichiometric mixture of $BaCO_3$ and TeO_2 heated to 550 °C for 3 days with intermediate re-grindings led to pure $BaTe_4O_9$.

The X-ray powder patterns (Philips PW1710 diffractometer, Cu Kα radiation, $\lambda = 1.5418$ Å, $T = 25 \pm 2$ °C) of hydrothermally made $BaTe_3O_7$ and ceramic $BaTe_4O_9$ were in excellent agreement with simulations based on the single-crystal structures, indicating phase purity and a high degree of crystallinity. TGA for $BaTe_3O_7$ and $BaTe_4O_9$ indicated no weight loss until ~850 °C, followed by continuous weight loss to 1000 °C, the limit of operation of the instrument. The IR spectra of $BaTe_3O_7$ and $BaTe_4O_9$ were consistent with their anhydrous nature and previous data for tellurites.[10]

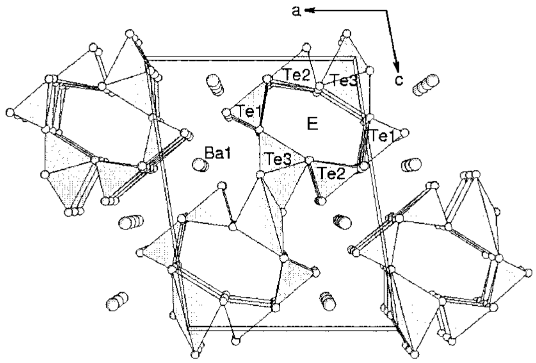

Figure 1. Polyhedral view down [010] of $BaTe_3O_7$ with the tellurium centers forming one $[Te_3O_7]^{2-}$ tube labeled. The empty tube is indicated by E.

Suitable single crystals of $BaTe_3O_7$ (transparent rod, 0.26 × 0.04 × 0.04 mm) and $BaTe_4O_9$ (transparent bar, 0.36 × 0.06 × 0.03 mm) were mounted on thin glass fibers and their structures were determined by standard X-ray methods[11] using a Bruker SMART1000 CCD diffractometer.

$BaTe_3O_7$ contains 11 unique atoms (1 Ba, 3 Te, 7 O), all of which occupy general positions. The oxygen atom geometries around Te1 and Te2 are well described as TeO_4 folded squares, as seen previously for similar groupings.[2] This geometry can be simply rationalized in VSEPR theory as an AX_4E trigonal bipyramid, with the lone pair occupying an equatorial position.[12] Te3 has less regular coordination, with three short (<2.00 Å), one intermediate length (2.24 Å), and one very long (2.56 Å) Te−O bond. The overall shape of this TeO_{3+1+1} grouping approximates to a distorted square-based pyramid. Bond valence sum (BVS)[13] values of 4.02, 4.05, and 4.15 for Te1, Te2, and Te3, respectively, are in good agreement with the expected 4.00. Six O atoms participate in Te−O−Te bridges ($\theta_{av} = 116.1°$) and one is terminal to Te1. All the O atoms also bond to one or more of the 11-coordinate barium cations [d_{av}(Ba−O) = 2.997 (3) Å]

The polyhedral connectivity in $BaTe_3O_7$ involves both vertex- and edge-sharing of the tellurite moieties. The Te1-, Te2-, and Te3-centered groups form 6-ring loops by way of Te−O−Te bridges (sequence: Te1, Te2, Te3, Te1, Te2, Te3). Stacking of these loops in the [010] direction leads to distinctive macroanionic $[Te_3O_7]^{2-}$ tubes (Figure 1). Despite their atom-to-atom dimensions of ~4.39 × 5.90 Å, they are completely empty. Although it is difficult

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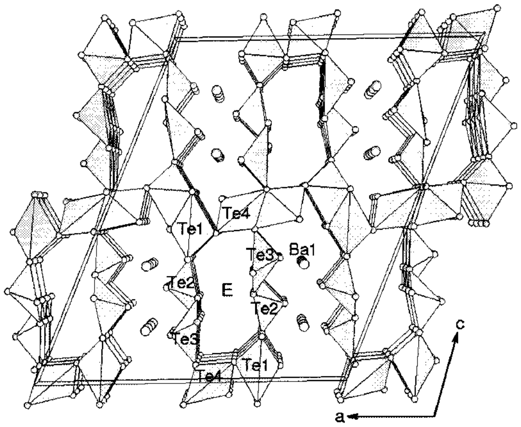

Figure 2. Polyhedral view down [010] of $BaTe_4O_9$ with the tellurium centers forming one $[Te_4O_9]^{2-}$ tube labeled. The empty tube is indicated by E.

to locate Te^{IV} lone pairs of electrons for non-pyramidal geometries,[14] it appears here that the Te1 and Te2 lone pairs point into the inside of the tube. Finally, the $[Te_3O_7]^{2-}$ tubes are cross-linked by way of edge-sharing through pairs of Te3−O7−Te3′ bonds to result in complex anionic sheets propagating in the (101) planes. The charge-balancing barium cations occupy inter-sheet sites.

$BaTe_4O_9$ contains 14 unique atoms (1 Ba, 4 Te, 9 O), all on general positions. Te1 and Te4 have (3 + 1) O atom coordination, similar to the situation[2] in $Co_2Te_3O_8$. Te2 and Te3 have four O atom neighbors in folded square conformations, with the axial Te−O bonds showing their usual lengthening relative to the equatorial bonds. BVS values of 3.90, 3.97, 3.96, and 3.87 result for Te1, Te2, Te3, and Te4, respectively. Five O atoms participate in Te−O−Te bridges ($\theta_{av} = 120.1°$), three are terminal to Te, and one (O7) is three-coordinate to Te neighbors. All the O atoms except O2, O7, and O8 also bond to one or more barium cations, which are nine coordinate [$d_{av} = 2.904$ (3) Å] in this structure.

The packing of the polyhedral building units in $BeTe_4O_9$ can be visualized in terms of infinite tubes of stoichiometry $[Te_4O_9]^{2-}$ propagating along the *b* direction. In this case, the tubes are built up from 8-ring loops (sequence: Te1, Te2, Te3, Te4, Te1, Te2, Te3, Te4). Stacking of the rings along the short *b* unit cell direction leads to infinite tellurite tubes (Figure 2). These units are highly squashed, with atom-to-atom dimensions of 3.49 × 7.97 Å, and the Te2 and Te3 lone pairs appear to point into the tubes. As in $BaTe_3O_7$, the $[Te_4O_9]^{2-}$ tubes in $BaTe_4O_9$ are cross-linked by edge-sharing. In $BaTe_4O_9$ the edge-sharing occurs by way of Te4−O7−Te4′ double bridges in the *c* direction and Te1−O1−Te1′ double bridges in the *a* direction to result in a three-dimensional Te/O network encapsulating the barium cations in [010] tunnels.

In summary, the title compounds demonstrate not just typical local distortions[5] of Te/O groupings, but a novel way to accommodate Te^{IV} lone-pair electrons in infinite, “self-contained” one-dimensional tubes. In fact, these tubes appear to be large enough to accommodate other chemical species such as H^+ or Li^+, which suggests the possibility of redox intercalation and/or ion-exchange chemistry for this type of structure. These processes seem unlikely in the title compounds where there are no easily reducible cations in the framework. However, extended tellurite networks incorporating species such as Mn^{3+} or Fe^{3+} might allow for the incorporation of lithium with concomitant reduction of M^{3+} to M^{2+} and we are continuing to investigate such systems.

Some time ago, Wroblewska et al.[9] prepared several barium tellurites by ceramic methods, but few structural details were elucidated. The unindexed powder pattern reported for $BaTe_4O_9$ (JCPDS card 36-0887) corresponds reasonably well to our data for the same phase. Interestingly, the phase $BaTe_2O_5$ reported by the same workers, which represents the $n = 2$ member of the $BaTe_nO_{2n+1}$ series, is possibly[15] monoclinic, with unit cell dimensions of $a = 19.85$ Å, $b = 4.38$ Å, $c = 7.39$ Å, and $\beta = 95.7°$ (JCPDS card 36-0886). This cell shape is similar to the “squashed” (small *b*) monoclinic cells found here for $BaTe_3O_7$ and $BaTe_4O_9$ and perhaps indicates that the putative $BaTe_2O_5$ possesses a similar structure to the title compounds. We are investigating the $n = 2$ material and endeavoring to prepare further members of this unusual family such as the $n = 5$ phase $BaTe_5O_{11}$.

Supporting Information Available: Crystallographic data for $BaTe_3O_7$ and $BaTe_4O_9$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) IR data for $BaTe_3O_7$: 786, 760, 695, 626, 577, 482, 422 cm^{-1}. IR data for $BaTe_4O_9$: 877, 759, 713, 682, 627 cm^{-1}.
(11) Crystal data for $BaTe_3O_7$: $M_r = 632.14$, monoclinic, $P2_1/n$ (No. 14), $a = 10.2765$ (6) Å, $b = 5.2510$ (3) Å, $c = 13.5499$ (8) Å, $\beta = 98.980$ (1)°, $Z = 4$, $R(F) = 0.030$, $wR2(F^2) = 0.071$. Crystal data for $BaTe_4O_9$: $M_r = 791.72$, monoclinic, $C2/c$ (No. 15), $a = 19.5354$ (10) Å, $b = 4.5099$ (2) Å, $c = 23.3021$ (12) Å, $\beta = 112.961$ (1)°, $Z = 4$, $R(F) = 0.039$, $wR2(F^2) = 0.095$.
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(15) This cell was established by the JCPDS Editor but assigned “0” (low) quality because of poor agreement between d_{obs} and d_{calc}.

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