The crystal chemistry of four thorium sulfates

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Four thorium sulfate compounds have been synthesized and characterized. [Th(SO4)2(H2O)7].2H2O (ThS1) crystallizes in space group P21/m, a = 7.2488(4), b = 12.1798(7), c = 8.0625(5) Å, β = 98.245(1)°; Na10[Th2(SO4)5(H2O)]2 3H2O (ThS2), Pna21, a = 17.842(2), b = 6.9317(8), c = 27.550(3) Å; Na2[Th2(SO4)5 (H2O)3].H2O (ThS3), C2/c, a = 16.639(2), b = 9.081(1), c = 25.078(3) Å, β = 95.322(2)°; [Th4(SO4)2(OH)2 (H2O)]2.2H2O (ThS4), Pnma, a = 18.2127(9), b = 11.1669(5), c = 14.4705(7) Å. In all cases the Th cations are coordinated by nine O atoms corresponding to SO4 tetrahedra, OH groups, and H2O groups. The structural unit of ThS1 is an isolated cluster consisting of a single Th polyhedron with two monodentate SO4 tetrahedra and seven H2O groups. A double-wide Th sulfate chain is the basis of ThS2. The structures of ThS3 and ThS4 are frameworks of Th polyhedra and sulfate tetrahedra, and each contains channels that extend through the framework. One of the Th cations in ThS3 is coordinated by a bidentate SO4 tetrahedron, and ThS4 is unusual in the presence of a pair of Th cations that share a polyhedral face.

1. Introduction

Thorium and uranium are the only actinides that occur in nature in appreciable quantities, and both can be the fuel of nuclear energy. Thorium-232 has a half-life of 1.4 × 10^10 years and can be used to breed 233U that is subsequently fissioned in a reactor. It is unlike most of the early actinides in that it is only stable in the tetravalent oxidation state. It is therefore a useful analog for the behavior of Np(V) and Pu(V) in the solid state.

Thorium is coordinated by 6–15 ligands in reported crystal structures. It has a strong tendency to form complexes with anions, and its crystal chemistry is relatively complex [1]. The interaction of Th with sulfate has been studied in solution [2] and the solid state [3–10], in part because Th sulfate complexes may be important for understanding the fate of Th in environments impacted by mining. To date there are seven strictly inorganic Th sulfate compounds. These exhibit considerable structural diversity, with structural units consisting of a cluster, a chain, and two frameworks of polyhedra.

2. Experimental

2.1. Syntheses

Caution! Thorium-232 is radioactive. Appropriate facilities and trained personnel are required for working with radioactive materials.

Th(NO3)4 · 4H2O (International Bio-Analytical Industries, Inc.), H2SO4 (LabChem, Inc.), Na2SO4 (Aldrich), and NaOH (Fisher) were used as received. Water was distilled and Millipore-filtered, 18.2 MΩ cm.

In a Teflon-lined 125-mL Parr acid digestion vessel, 0.7500 g of Th(NO3)4 · 4H2O and 20.6 mL H2O were combined and the pH was adjusted to 4.0 by adding 1 M NaOH. The solution was heated to 65 °C for 24 h in a mechanical convection oven. The result was a clear colorless solution hereafter designated solution-1. In a glass beaker 13.8049 g of Th(NO3)4 · 4H2O was dissolved in 50.0 mL H2O at room temperature, giving a clear solution hereafter referred to as solution-2.
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Table 1
Crystallographic data for ThS1, ThS2, ThS3, and ThS4.

<table>
<thead>
<tr>
<th></th>
<th>ThS1 [Th(II)(SO4)(H2O)2] · 2H2O</th>
<th>ThS2 Na10Th2(SO4)6(H2O)2 · 3H2O</th>
<th>ThS3 Na4Th2(II)(SO4)3(H2O)2 · H2O</th>
<th>ThS4 [Th(II)(SO4)2(OH)2(H2O)2] · 2H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>7.248(8)</td>
<td>17.842(2)</td>
<td>16.639(2)</td>
<td>18.2127(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.179(7)</td>
<td>6.9317(8)</td>
<td>9.081(1)</td>
<td>11.1669(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.0625(5)</td>
<td>27.550(3)</td>
<td>25.078(3)</td>
<td>14.4705(7)</td>
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<tr>
<td>β (deg)</td>
<td>98.245(1)</td>
<td>90</td>
<td>95.322(2)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>704.47(7)</td>
<td>3405.3(4)</td>
<td>3772.8(8)</td>
<td>2943.0(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/m</td>
<td>P1/a2</td>
<td>C2/c</td>
<td>Pnma</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>R(000)</td>
<td>552</td>
<td>3048</td>
<td>3792</td>
<td>3104</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>10.966</td>
<td>9.542</td>
<td>16.47</td>
<td>20.79</td>
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<tr>
<td>Dv (g/cm³)</td>
<td>2.764</td>
<td>3.194</td>
<td>3.712</td>
<td>3.974</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.12 × 0.11 × 0.090</td>
<td>0.090 × 0.085 × 0.075</td>
<td>0.15 × 0.13 × 0.10</td>
<td>0.16 × 0.12 × 0.10</td>
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<tr>
<td>Radiation</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
</tr>
<tr>
<td>T(K)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
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<tr>
<td>Framework (deg)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
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<tr>
<td>Count time per frame (s)</td>
<td>10</td>
<td>120</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>θ range (deg)</td>
<td>2.55–28.68</td>
<td>2.28–31.96</td>
<td>2.46–27.89</td>
<td>2.56–34.52</td>
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<td>Reflections collected</td>
<td>8430</td>
<td>44,074</td>
<td>25,726</td>
<td>57,974</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1807</td>
<td>11,722</td>
<td>10,966</td>
<td>6405</td>
</tr>
<tr>
<td>Unique Fσ&gt; 4σr</td>
<td>1746</td>
<td>8247</td>
<td>3875</td>
<td>5278</td>
</tr>
<tr>
<td>R₁</td>
<td>0.0133</td>
<td>0.0322</td>
<td>0.0722</td>
<td>0.0648</td>
</tr>
<tr>
<td>S</td>
<td>1.05</td>
<td>1.02</td>
<td>1.04</td>
<td>1.03</td>
</tr>
</tbody>
</table>

\[ R₁ = \frac{\sum F_o - |F_c| \sum F_w \sin(2θ)}{\sum F_o \sin(2θ)} = \left\{ \sum w(F_o^2 - F_c^2) \right\}^{1/2}.

Table 2
Selected interatomic distances in the structure of ThS1.*

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(1)–O(3)</td>
<td>2.3645(18)</td>
<td>S(1)–O(2)</td>
<td>1.464(2)</td>
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<tr>
<td>Th(1)–O(3)</td>
<td>2.3646(18)</td>
<td>S(1)–O(8)</td>
<td>1.4659(19)</td>
</tr>
<tr>
<td>Th(1)–O(5)</td>
<td>2.4474(19)</td>
<td>S(1)–O(4)</td>
<td>1.4664(18)</td>
</tr>
<tr>
<td>Th(1)–O(5)</td>
<td>2.4474(19)</td>
<td>S(1)–O(3)</td>
<td>1.4854(18)</td>
</tr>
<tr>
<td>Th(1)–O(7)</td>
<td>2.4775(19)</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
</tr>
<tr>
<td>Th(1)–O(7)</td>
<td>2.4775(19)</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
</tr>
<tr>
<td>Th(1)–O(10)</td>
<td>2.483(3)</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
</tr>
<tr>
<td>Th(1)–O(6)</td>
<td>2.492(3)</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
</tr>
<tr>
<td>Th(1)–O(1)</td>
<td>2.509(3)</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
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<tr>
<td>S(1)–O(1)</td>
<td>2.451</td>
<td>S(1)–O(1)</td>
<td>1.470</td>
</tr>
</tbody>
</table>

* Symmetry transformations: (a) x, –y+1/2, z, (b) –x+2, –y, –z, (c) –x+2, y+1/2, –z, and (d) –x+2, –y, –z+1.

[Th(II)(SO4)(H2O)2] · 2H2O, **ThS1**: Thorium nitrate tetrahydrate (0.4419 g) was dissolved in 2 mL of 1.5 M H2SO4. The solution was covered with paraffin with a small hole to allow slow evaporation. After 2 weeks blocky crystals formed and were recovered for analysis.

Na10Th2(SO4)6(H2O)2 · 3H2O, **ThS2**: Solution-1 (0.250 mL) and Na2SO4 (0.146 g) were combined and heated in a 5 mL polypropylene vial inside a 125 mL Teflon-lined Parr acid digestion vessel that was heated at 100 °C for 24 h. Twenty-five milliliters of H2O was placed in the outer liner of the vessel to provide counter pressure. The resulting crystal-free solution was transferred to a glass vial that was capped. After several months, bladed crystals appeared in solution and were harvested for analysis.

Na4Th2(II)(SO4)3(H2O)2 · H2O, **ThS3**: Solution-1 (0.250 mL) and H2SO4 (0.100 mL concentration) were combined and heated at 100 °C for 24 h in a 5 mL polypropylene vial that was placed inside a 125 mL Teflon-lined Parr acid digestion vessel. Twenty-five milliliters of H2O was placed in the outer liner of the vessel to provide counter pressure during heating. After heating the resulting crystal-free solution was transferred to a glass vial that was capped. After several months bladed crystals appeared in solution and were harvested for analysis.

[Th(II)(SO4)2(OH)2(H2O)2] · 2H2O, **ThS4**: Solution-2 (1.000 mL) was combined with 1.000 mL of 0.200 M H2SO4. The resulting solution was heated in a 23 mL Parr acid digestion vessel at 180 °C for 5 days. The crystal-free solution was then transferred to a glass vial that was capped. After several weeks blocky crystals appeared in solution and were recovered for analysis.

2.2. Crystallographic studies

A suitable single crystal of each compound without evident twinning or inclusions was selected using a polarized-light microscope and was glued to a tapered glass fiber. Spheres of X-ray diffraction data were collected using an APEX (ThS2 and ThS4) or APEX II (ThS1 and ThS3) detector mounted on a three-circle goniometer using graphite-monochromated MoKα radiation. The data were collected with frame widths of 0.3 ° in φ and 10 (or 120) s spent counting per step. Data were integrated and corrected for Lorentz, background, and polarization effects for each crystal using the APEX II software [11]. Data were corrected for absorption using SADABS [12], and the structures were solved and refined using the Bruker SHELXL v6.12 [13] software. The final model for ThS1 included H atoms. These were located in difference-Fourier maps and were refined with the constraint that O–H bond lengths be ≈ 0.96 Å. The displacement parameters of all non-H atoms were refined anisotropically for all compounds. H atoms were not located for the structures of ThS2, ThS3, or ThS4; O atoms in these structures were assigned as O2−, OH−, or H2O on the basis of the bond-valence sums incident upon these positions. Structures were examined in search of higher symmetry using PLATON as implemented in WinGX [14]. Crystallographic data for all four compounds is shown in Table 1, and selected interatomic distances are in Tables 2–5. Full details of the crystal structures are given in the supporting information.
2. Chemical analysis

A SensIR technology IllumintIR FT-IR Microspectrometer with a ContactIR diamond attenuated total reflectance (ATR) IR objective was used to collect data ranging from 650 to 4000 cm⁻¹ for each compound. In each case a crystal was placed on a glass slide and was contacted by the ATR objective. The spectra are in the supporting information.

2.4. Chemical analysis

Crystals of ThS3 were dissolved in 5% HNO3 and the resulting solution was analyzed using a Perkin-Elmer Optima 2000DV inductively coupled-plasma optical-emission-spectrometer. The analysis provided a Th:S:Na ratio of 2:5.06:2.09, respectively.

3. Results

The cation coordination polyhedra in the four compounds under study are similar. Each Th cation is coordinated by nine O atoms that belong to OH⁻, H2O, or (SO4)²⁻ groups. Polyhedral geometries range from monocapped square antiprisms (ThS3 and ThS4) to tricapped trigonal prisms (ThS1, ThS2, ThS3, and ThS4). The Th–O bond lengths range from 2.313(6) to 2.720(6) Å, and the averages for individual polyhedra range from 2.438 to 2.460 Å. Each of the SO₄²⁻ cations are tetrahedrally coordinated by four O atoms, with bond lengths ranging from 1.411(11) to 1.508(11) Å across the structures, and individual tetrahedral averages ranging from 1.447 to 1.487 Å.

Whereas the local cation coordination environments are similar in the compounds under study, their extended structures reveal considerable diversity. ThS1 is the simplest of these structures, and it contains only single crystallographically distinct Th and S cations. Two monodentate SO₄ tetrahedra, as well as seven H2O groups, coordinate each Th cation. The result is a small electroneutral cluster of composition [Th(H2O)7(SO4)2] (Fig. 1). A single crystallographically unique H2O group is located between the thorium sulfate clusters, where it is held in place by H bonding. An extensive network of H bonds extend from the H2O groups of the Th polyhedra to O atoms of SO4 tetrahedra in other clusters, as well as to the interstitial H2O group. Each of the terminal O atoms of the SO4 tetrahedra are H bond acceptors with H···O bond lengths in the range 1.8–2.0 Å. The O(8) anion accepts bonds from H(1) and H(9), O(4) accepts bonds from H(2) and H(4), and O(2) accepts bonds from H(5) and H(6). Note that these H bonds, together with the S···O bonds, result in bond-valence sums of ~2.0 valence units at the O position in each case, consistent with their assignment as O²⁻ anions.

There are two crystallographically distinct Th cations in ThS2, as well as nine sulfate tetrahedra. One H2O group, four O atoms of two bidentate SO4 tetrahedra, and four O atoms of monodentate SO4 tetrahedra coordinate each Th cation. Each of the S(1), S(8), and S(9) sulfate tetrahedra bridge between two ThO4 polyhedra by sharing a vertex with each of them. The S(2), S(3), S(4), and S(5) tetrahedra are bidentate to Th cations. The remaining tetrahedra, S(6) and S(7), share only a single vertex with a ThO4 polyhedron. Thorium sulfate chains extending along [010] result from the extensive vertex-sharing between the SO4 tetrahedra and Th polyhedra (Fig. 2). These chains are linked into an extended structure through ten symmetrically distinct Na cations. There are also three H2O groups that bond only to Na.

ThS3 contains two crystallographically distinct ThO4 polyhedra. Th(1) is coordinated by one bidentate S(1)O4 tetrahedron, by six monodentate SO4 tetrahedra, and by one H2O group. The Th(2) cation is coordinated by seven monodentate SO4 tetrahedra.
and two H₂O groups. There are five crystallographically distinct sulfate tetrahedra. The S(1)O₉ tetrahedron shares an edge with the Th(1) polyhedron, and a single vertex with another Th(1) polyhedron. Each of the S(2) through S(5) tetrahedra share three of their vertices with three different Th polyhedra. The S(2) position is split over two sites, each of which are tetrahedrally coordinated and only one of which can be occupied locally.

The linkages between sulfate tetrahedra and Th polyhedra in ThS₃ result in a complex framework structure (Fig. 3). Within this, layers parallel to (101) are connected through S(1)O₉ tetrahedra. Elongated channels extend through the structure between these layers, and contain disordered Na cations. Additional channels extend along [001], and are bounded by non-bridging O atoms of SO₄ tetrahedra. The framework has the composition Th₂(3)SO₄(5)H₂O and requires four Na cations on general positions to provide charge-balance. Three of these Na cations are specifically localized in the channels to be included in the structure refinement. ICP-OES analysis of dissolved crystals of ThS₃ gave atomic ratios of Th:S:Na of 2.506:2.09, consistent with the assigned composition Na₃Th₂(3)SO₄(5)H₂O₃ and charge-balance requirements.

There are three crystallographically distinct ThO₉ polyhedra in ThS₄, of which Th(1)O₉ is a distorted monocapped square antiprism and Th(2)O₉ and Th(3)O₉ are tricapped trigonal prisms. The Th(1)O₉ polyhedra are unusual because a pair of them share a face defined by the O(15), O(19), and O(20) hydroxyl groups. The Th(1)–Th(1) separation is 3.8969(3) Å, indicating no metal–metal bonding interaction is present. In addition, each Th(1) cation is coordinated by five monodentate SO₄ tetrahedra and a single H₂O group. Both the Th(2) and Th(3) cations are coordinated by seven monodentate SO₄ tetrahedra and two H₂O groups. There are four crystallographically distinct SO₄ tetrahedra, two of which share three of their vertices with different ThO₉ polyhedra. The remaining two SO₄ tetrahedra [S(3), S(4)] each share all four of which their vertices with four different ThO₉ polyhedra.

The direct linkage between pairs of Th(1)O₉ polyhedra, as well as linkages through SO₄ tetrahedra, result in an electroneutral framework (Fig. 4). Elongated channels extend along [010] and contain H₂O.
4. Discussion

The structural topologies of the four hydrous Th sulfates reported herein, and those reported by other researchers, are impacted most by the details of the sharing of polyhedral elements between the sulfate and Th polyhedra. In all of these structures Th cations are coordinated by sulfate tetrahedra. Furthermore, all of the sulfate tetrahedra coordinate between one and four Th polyhedra; none are isolated. The details of the structures are therefore dependent on both the Th:S ratio and the amount of H$_2$O that is incorporated into the coordination polyhedra about the Th cations.

The cluster structure unit in ThS$_1$ is unique in tetravalent actinide (An) materials. More than 25 An(IV) compounds have structures that consist of finite clusters, and several contain tetrahedrally coordinated hexavalent cations. The structure of Th(SO$_4$)$_2$(H$_2$O)$_8$ contains Th cations that are coordinated by two bidentate SO$_4$ tetrahedra and six H$_2$O groups, resulting in a coordination number of 10 [3]. In K$_6$Th(MoO$_4$)$_3$, the Th coordination number is seven and the cation is coordinated by one bidentate and five monodentate MoO$_4$ tetrahedra [15]. In K$_5.5$(H$_2$O)$_3$Np(SO$_4$)$_3$(H$_2$O), the Np(IV) cation is coordinated by five bidentate SO$_4$ tetrahedra, giving a coordination number of 10 [16].

There are at least a dozen An(IV) compounds that have structural units that consist of chains, as in ThS$_2$. Several of these contain tetrahedrally coordinated hexavalent cations. For example, the chain in K$_2$Th(MoO$_4$)$_3$ is denser than that in ThS$_2$, each ThO$_7$ polyhedron shares two of its edges with adjacent ThO$_7$ polyhedra, and each MoO$_4$ tetrahedron is two-connected to the chain [17]. In K$_4$Th(SO$_4$)$_4$(H$_2$O)$_2$, the coordination number of the Th cations is nine (as in ThS$_2$), and each Th cation is coordinated by one bidentate and five monodentate SO$_4$ tetrahedra, as well as two H$_2$O groups [18]. This chain differs from that in ThS$_2$ most notably in that two sulfate tetrahedra bridge between each pair of ThO$_9$ polyhedra in K$_4$Th(SO$_4$)$_4$(H$_2$O)$_2$, whereas in ThS$_2$ ThO$_9$ polyhedra are bridged by only a single sulfate tetrahedron. In Na$_{10}$Np$_2$(SO$_4$)$_3$Th(H$_2$O)$_3$(H$_2$O)$_3$, in contrast, three sulfate tetrahedra bridge between each Th polyhedron along the chain length [5]. The structure of Na$_{10}$Np$_2$(SO$_4$)$_3$(H$_2$O)$_4$ [19] contains one less H$_2$O group than ThS$_2$, but otherwise is identical to ThS$_2$, providing an...
example of complex Th and Np(IV) compounds that are isostructural.

Compounds ThS3 and ThS4 join a family of more than 80 framework structures that contain An(IV) cations. Here we focus discussion on the most closely related structures that contain tetrahedrally coordinated hexavalent cations. Whereas ThS3 and ThS4 contain channels that extend through the framework, they are small in comparison to those in Th3(SO4)6(H2O)6•C12H2O, which are 11.5 Å in two directions [10]. In this porous structure each of the Th cations are coordinated by seven monodentate SO4 tetrahedra and two H2O groups, and the SO4 tetrahedra are connected to either three of four Th cations. The compound Th(Oh)2(SO4) has a close-knit framework that contains chains of edge-sharing ThO4 polyhedra [9]. The Th cations are coordinated by four monodentate SO4 tetrahedra and four OH groups.

Several Th and U(IV) molybdates with framework structures have been reported. Three of these, CdTh(MoO4)3, CuU(MoO4)3, and Th(MoO4)2, have similar frameworks with channels extending along the [001] direction [20,21,22]. In CdTh(MoO4)3 and CuU(MoO4)3, the Cd and Cu cations are located within these channels, where they are octahedrally coordinated by six monodentate MoO4 tetrahedra. In Th(MoO4)2, half of the channel sites (relative to the other two compounds) are occupied by Th in a usual octahedral coordination. The non-channel Th cations in the structures are coordinated by nine monodentate MoO4 tetrahedra.

ThMo2O8 and UMo2O8 have dense frameworks in which each An(IV) cation is coordinated by eight monodentate MoO4 tetrahedra, and each tetrahedron shares all four of its vertices with An(IV) polyhedra [23,24]. The compound K2Th(MoO4)3 has a framework structure with relatively small channels that extend along [010] [25]. Each Th cation is coordinated by eight monodentate MoO4 tetrahedra, and each tetrahedron shares vertices with two Th polyhedra. Cu2Th4(MoO4)9 has a close-knit framework in which each Th cation is coordinated by nine monodentate MoO4 tetrahedra, and each tetrahedron shares all four of its vertices with different Th polyhedra [26]. In Th(CrO4)(IO3)2, the dense framework contains Th cations that are coordinated by three monodentate CrO4 tetrahedra and six IO3 pyramids, and each tetrahedron is connected to four Th polyhedra [27].

Relative to other framework structures containing An(IV) cations, ThS3 is unusual in that one of the Th polyhedra has a bidentate SO4 group. In the case of ThS4, the presence of a pair of face-sharing ThO3 polyhedra is novel, and leads to a denser framework than would otherwise be achieved.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.04.024.

References


Fig. 4. Representations of the structure of ThS4: (a) projection along [010], (b) projection along [100], and (c) face sharing between two Th polyhedra. Legend as in Fig. 1 except O and Th atoms are shown as red and green balls, respectively (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).


