

MS15-1-10 Closing Some Gaps of Knowledge: Single Crystals of $\text{Tm}_2\text{O}[\text{SiO}_4]$ with the B-Type Structure #MS15-1-10P. Djendjur ¹, S. Greiner ¹, T. Schleid ¹¹University of Stuttgart / Institute for Inorganic Chemistry - Stuttgart (Germany)**Abstract**

Lanthanoid oxosilicates and their derivatives show a huge variety of compositions and structures. Since many solid-state reactions take place in glassy silica ampoules, a rather big proportion of side products from these reactions tend to yield oxosilicate derivatives. Compounds of the formula type $\text{Ln}_2\text{O}[\text{SiO}_4]$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Ho} - \text{Lu}$) realize two different structure types. The $\text{Gd}_2\text{O}[\text{SiO}_4]$ - or A-type structure is adopted by representatives all over the whole lanthanoid series ($\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Ho} - \text{Tm}$ and Lu) ^[1-6] and exhibits isolated $[\text{SiO}_4]^{4-}$ tetrahedra in combination with a porous network

of distorted $[\text{OLn}_4]^{10+}$ tetrahedra connected via edges and corners forming $\infty^2\{[\text{O}(\text{Ln}1)_{1/1}(\text{Ln}2)_{3/3}]^{4+}\}$ layers, which spread out parallel to the (100) plane. Another structure type is represented by the $\text{Yb}_2\text{O}[\text{SiO}_4]$ - or B-type arrangement, which is so far only known with the heavier lanthanoids ($\text{Ln} = \text{Er}, \text{Yb} - \text{Lu}$) ^[7-9]. In this work, we present another representative of these B-type lanthanoid(III) oxide oxosilicates, namely $\text{Tm}_2\text{O}[\text{SiO}_4]$, which closes the gap in the short $\text{Ln}_2\text{O}[\text{SiO}_4]$ series with $\text{Ln} = \text{Er} - \text{Lu}$. It crystallizes in the monoclinic space group $C2/c$ with the lattice parameters $a = 1432.74(11)$ pm, $b = 668.52(5)$ pm, $c = 1033.67(8)$ pm, $\beta = 122.183(3)^\circ$ and $Z = 8$ (CSD-2169113).

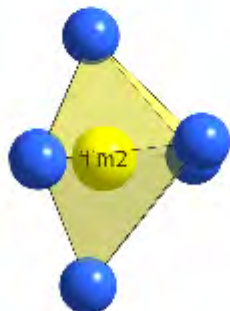
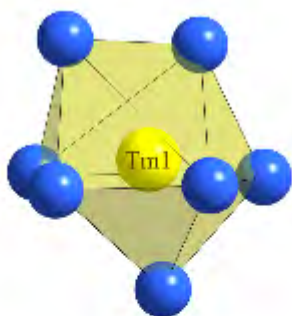
The crystal structure consists of two crystallographically different Tm^{3+} cations (Figure 1). $(\text{Tm}1)^{3+}$ is surrounded by seven oxygen atoms to form a capped octahedron, whereas $(\text{Tm}2)^{3+}$ has a distorted octahedron with only six oxygen atoms as coordination sphere. With this in mind, it becomes clear, why the B-type structure can only be found with representatives of the later part of the lanthanoid series, offering rather small coordination spheres for both Ln^{3+} cations. Like in the A-type structure, silicon is surrounded by four of the five distinct oxygen atoms to form $[\text{SiO}_4]^{4-}$ tetrahedra ($d(\text{Si}-\text{O}) = 161 - 164$ pm), which remain isolated from one another. The single remaining oxygen atom (O5) is coordinated in a distorted tetrahedral manner by four Tm^{3+} cations, building $[\text{OTm}_4]^{10+}$ units, which are connected via common *trans*-oriented edges

to two neighbouring $[\text{OTm}_4]^{10+}$ units to form undulated $\infty^1\{[\text{O}(\text{Tm}1)_{2/2}(\text{Tm}2)_{2/2}]^{4+}\}$ strands propagating parallel to the [001] direction (Figure 2).

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Coordination polyhedra of (Tm1)³⁺ and (Tm2)³⁺.



Unit cell of the B-type structure of Tm₂O[SiO₄].

