Crystal Structure of B-Type $Tm_2Si_2O_7$ ($\equiv Tm_4[Si_3O_{10}][SiO_4]$)

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Single crystals of B-type thulium oxodisilicate $Tm_2Si_2O_7$ were obtained by the reaction of Tm, S and RbCl with the wall of a silica tube in an attempt to synthesize ternary alkali-metal thulium sulfides (*e.g.* $Rb_3Tm_7S_{12}$). It crystallizes triclinically in space group $P\bar{1}$($a = 655.91(5)$, $b = 659.04(5)$, $c = 1195.32(9)$ pm, $\alpha = 94.361(8)$, $\beta = 91.102(8)$, $\gamma = 92.005(8)°$), with four formula units of $Tm_2Si_2O_7$ per unit cell. Instead of pyro-anionic $[Si_2O_7]^{6-}$ groups the title compound contains both *ortho*-silicate tetrahedra $[SiO_4]^{4-}$ and *catena*-trisilicate units $[Si_3O_{10}]^{8-}$. Therefore the formula $Tm_4[Si_3O_{10}][SiO_4]$ ($Z = 2$) appears more adequate. The four crystallographically independent Tm^{3+} cations show coordination numbers from six to eight with distorted octahedral, bicapped trigonal prismatic and square antiprismatic oxygen coordination spheres.

Key words: Lanthanides, Thulium, Oxosilicates, Crystal Structure

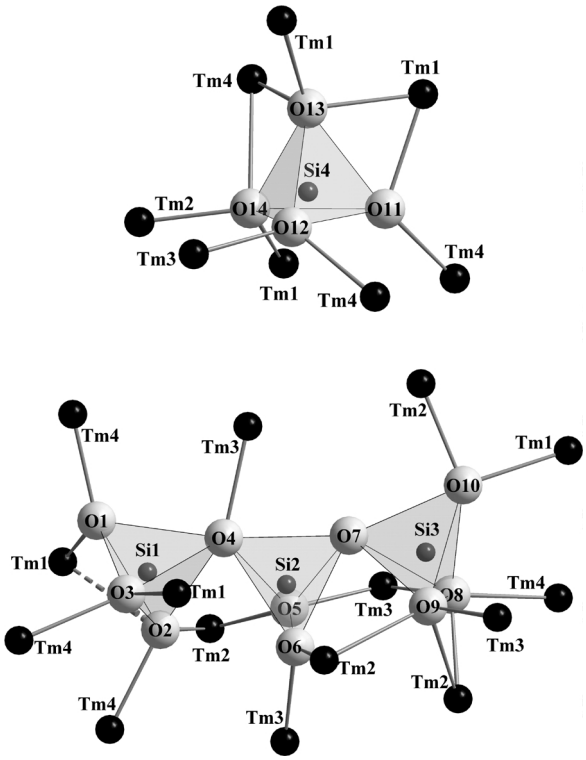

Fig. 1. Coordination of eight Tm^{3+} cations around the *ortho*-silicate anion $[SiO_4]^{4-}$ (*above*) and the *catena*-trisilicate unit $[Si_3O_{10}]^{8-}$ carrying fifteen Tm^{3+} cations (*below*).

Introduction and Experimental Results

Since the beginning of the 1970's seven different structure types (A – G type) of the composition $M_2Si_2O_7$ (M = rare-earth metal) are well known in the literature [1]. At the end of the 1990's this range has been extended by the discovery of the so-called H-type [2], I-type [3] and K-type structures [4]. Except the B and the I type all of these compounds contain discrete pyro-anionic oxodisilicate units $[Si_2O_7]^{6-}$ with either linear (C and D type) or bent Si–O–Si bridges (A, E, F, G, H and K type). The crystal structure of I-type $La_2Si_2O_7$ consists of two crystallographically different *ortho*-silicate tetrahedra $[SiO_4]^{4-}$ and one horseshoe-shaped *catena*-tetrasilicate unit $[Si_4O_{13}]^{10-}$. For B-type rare-earth oxodisilicates with M = Eu – Er and Y [5] it was already known, that their structure is built of *ortho*-silicate and *catena*-trisilicate units according to $M_4[Si_3O_{10}][SiO_4]$. In the literature [6], the field has been extended to include the thulium compound as well. However, B-type $Tm_2Si_2O_7$ was specified as a high-pressure form, and for the crystal-structure refinement only X-ray powder-diffraction data were used [6].

Now, in an attempt to synthesize ternary rubidium thulium sulfides (*e.g.* $Rb_3Tm_7S_{12}$) using elemental thulium and sulfur in rubidium chloride as agent and flux, single crystals of $Tm_2Si_2O_7$ formed at normal pressure. At a temperature of 900 °C (7d) the mixture reacted with the silica ampoule (SiO_2) used as container, yielding hard, pale yellow, needle-shaped crystals which have been identified by single-crystal X-ray diffraction [7].

Structure Description

B-type $Tm_2Si_2O_7$ crystallizes triclinically (space group $P\bar{1}$) with two formula units per unit cell for

Table 1. Atomic positions and equivalent isotropic displacement parameters of B-type $Tm_2Si_2O_7$ (all atoms occupy the Wyckoff position *2i*).

Atom	x/a	y/b	z/c	U_{eq}[a)]/pm^2
Tm1	0.45259(5)	0.17011(5)	0.88461(3)	44(1)
Tm2	0.38426(5)	0.40792(5)	0.64224(3)	47(1)
Tm3	0.12913(5)	0.28396(5)	0.36671(3)	60(1)
Tm4	0.17095(5)	0.67298(5)	0.89149(3)	55(1)
Si1	0.9873(3)	0.1641(3)	0.8254(2)	38(4)
Si2	0.8788(3)	0.2238(3)	0.5948(2)	36(4)
Si3	0.3569(3)	0.8734(3)	0.6203(2)	34(4)
Si4	0.3438(3)	0.3522(3)	0.1151(2)	33(4)
O1	0.1480(8)	0.0105(8)	0.8751(5)	50(10)
O2	0.1139(9)	0.3644(8)	0.7879(5)	73(11)
O3	0.7994(8)	0.2037(8)	0.9069(5)	65(11)
O4	0.9027(9)	0.0652(8)	0.6947(5)	63(10)
O5	0.0871(8)	0.3264(8)	0.5519(5)	67(11)
O6	0.7260(8)	0.4025(8)	0.6233(5)	60(10)
O7	0.2137(9)	0.9269(9)	0.5120(5)	82(11)
O8	0.2134(8)	0.7157(8)	0.6868(5)	69(11)
O9	0.5400(8)	0.7260(8)	0.5754(5)	76(11)
O10	0.4277(8)	0.0831(8)	0.6889(5)	61(10)
O11	0.2650(9)	0.4161(8)	0.9951(5)	80(11)
O12	0.1507(8)	0.2870(8)	0.1863(5)	58(10)
O13	0.5007(8)	0.1683(8)	0.0809(5)	46(10)
O14	0.4955(8)	0.5191(8)	0.1859(5)	56(10)

a) $U_{eq} = 1/3(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha)$.

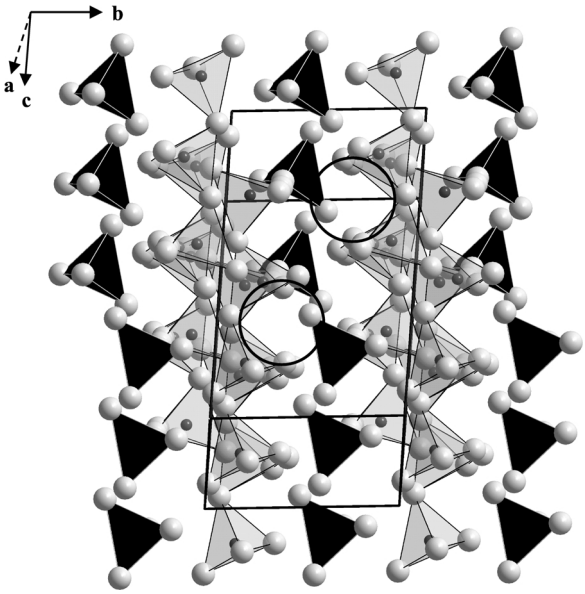

Fig. 2. Portion of the oxosilicate partial structure viewed along [−101] (black tetrahedra: *ortho*-silicate units $[SiO_4]^{4-}$; transparent tetrahedra: *catena*-trisilicate units $[Si_3O_{10}]^{8-}$; black circles: interstices wherein Tm^{3+} cations are situated).

Table 2. Selected internuclear distances (d/pm) and angles (∡/grd) for B-type $Tm_2Si_2O_7$.

		d/pm			d/pm			d/pm
Tm1	– O1	222.2	Tm3	– O12	216.5	Si1	– O3	160.2
	– O3	228.6		– O5	223.4		– O1	162.2
	– O14	229.0		– O6	223.8		– O2	163.1
	– O13	232.8		– O9	227.0		– O4	172.0
	– O13’	236.2		– O8	232.4	Si2	– O6	159.4
	– O10	236.7		– O4	236.2		– O5	161.3
	– O11	240.1					– O7	164.9
	– O2	*287.0*					– O4	165.4
						Si3	– O10	160.2
Tm2	– O14	219.9	Tm4	– O1	225.8		– O8	163.8
	– O5	223.9		– O11	226.8		– O9	164.4
	– O6	225.8		– O2	231.4		– O7	165.2
	– O10	227.9		– O12	232.1	Si4	– O12	160.4
	– O8	238.2		– O13	236.7		– O11	160.6
	– O9	249.2		– O3	248.6		– O14	163.3
	– O2	253.3		– O8	250.4		– O13	165.0
	– O9’	274.3		– O14	270.9			
		∡/grd		∡/grd			∡/grd	
O2 – Si1 – O4		98.6	O4 – Si2 – O7		102.5	O8 – Si3 – O9		101.7
O1 – Si1 – O2		108.5	O5 – Si2 – O7		105.9	O7 – Si3 – O8		104.3
O1 – Si1 – O4		108.9	O5 – Si2 – O6		107.4	O7 – Si3 – O10		108.3
O3 – Si1 – O4		110.8	O6 – Si2 – O7		109.7	O7 – Si3 – O9		109.0
O1 – Si1 – O3		112.2	O4 – Si2 – O6		114.2	O9 – Si3 – O10		116.3
O2 – Si1 – O3		116.9	O4 – Si2 – O5		116.5	O8 – Si3 – O10		116.5
Si1 – O4 – Si2		118.0	O13 – Si4 – O14		101.8	O12 – Si4 – O14		112.2
Si2 – O7 – Si3		129.9	O11 – Si4 – O13		102.8	O12 – Si4 – O13		115.3
			O11 – Si4 – O12		109.0	O11 – Si4 – O14		115.6

the formula $Tm_4[Si_3O_{10}][SiO_4]$. Thus, it is obvious that four crystallographically independent Tm^{3+} are distinguished in the crystal structure (Table 1). The coordination polyhedra of Tm1 and Tm2 can be described as trigonal prisms that are bicapped by oxide anions (1+1-fold for Tm1, CN = 7+1, and 2-fold for Tm2, CN = 8). Tm3 shows an environment of six O^{2-} anions arranged in the shape of a distorted octahedron. Finally, the Tm4 cations are surrounded by eight oxygen neighbours in a geometry approaching a trigon-dodecahedron. As already mentioned, the crystal structure of B-type $Tm_2Si_2O_7$ does not consist of pyro-anionic oxodisilicate units $[Si_2O_7]^{6-}$ but of *ortho*-silicate tetrahedra $[SiO_4]^{4-}$ combined with *catena*-trisilicate units $[Si_3O_{10}]^{8-}$ instead, which are built of three vertex-sharing $[SiO_4]$ tetrahedra. Regarding the discrete $[SiO_4]^{4-}$ unit (Fig. 1, *above*), the Si–O distances and O–Si–O angles with values of 160 – 165 pm and 102 – 117° (Table 2) are comparable to almost any other *ortho*-oxosilicate unit known in solid-state compounds. The *catena*-trisilicate unit (Fig. 1, *below*) is surrounded by fifteen Tm^{3+} cations exhibiting two minor peculiarities. The $(Tm2)^{3+}$ and $(Tm3)^{3+}$ cations interconnect two of the three $[SiO_4]$ tetrahedra *via* terminal oxide anions, and one of the bridging oxygen atoms (O4) is bonded to a $(Tm3)^{3+}$ cation, which is not a very common feature among vertex-sharing tetrahedra. This can be explained by comparing the two Si–O–Si bridging angles at O4 and O7. Whereas the Si2–O7–Si3 angle with a value of 130° corresponds very well to common pyro-anionic bridging angles [8], the Si1–O4–Si2 bridge exhibits an angle of about 118° only, which is unusually small. A possible interpretation of those two rather different angles is a phase transition from E-type to B-type rare-earth oxodisilicates described in the literature [1]. E-type $M_2[Si_2O_7]$ representatives provide the same existence range and similar cell volumes as B-type disilicates, but they really consist of pyro-anionic disilicate units $[Si_2O_7]^{6-}$. In the E-type $M_2[Si_2O_7]$ structure, one of two vicinal disilicate units breaks up to form an *ortho*-silicate anion $[SiO_4]^{4-}$ and a $[SiO_3]^{2-}$ fragment. The latter joins the remaining, still intact $[Si_2O_7]^{6-}$ anion to become part of the *catena*-trisilicate unit with an approximately *all*-eclipsed conformation of the $[SiO_4]$ tetrahedra involved and one rather small Si–O–Si bridging angle of 118° in the B-type $M_2Si_2O_7$ members. This presents only low sterical hindering and enough space for a coordinating rare-earth M^{3+} cation is left. Considering the whole structure of B-type $Tm_2Si_2O_7$, *ortho*- and *catena*-trisilicate units are alternatingly stacked in layers parallel (−101) (Fig. 2). The Tm^{3+} cations are situated in the interstices (emphasized by black circles in Fig. 2) and connect the *ortho*-silicate and *catena*-trisilicate packages.

Acknowledgement

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[7] The measurement of the intensity data set of B-type $Tm_2Si_2O_7$ has been carried out at room temperature with a Stoe-IPDS diffractometer using Mo-K_α radiation (graphite monochromator, $\lambda = 71.07$ pm). *Crystal data:* triclinic, space group $P\bar{1}$ (no. 2), $a = 655.91(5)$, $b = 659.04(5)$, $c = 1195.32(9)$ pm, $\alpha = 94.361(8)$, $\beta = 91.102(8)$, $\gamma = 92.005(8)°$, $V_m = 77.499$ cm^3/mol, $\rho_{cal} = 6.530$ g/cm^3; $\theta_{max} = 27.5°$ ($\pm h = \pm k = 8$, $\pm l = 15$), 9146 measured reflections (2367 independent, $R_{int} = 0.038$, $R_\sigma = 0.029$; 2308 with $|F_o| > 4\sigma(F_o)$, numerical absorption correction ($\mu = 34.69$ mm^{-1}) using the program HABITUS (W. Herrendorf and H. Bärnighausen, Karlsruhe 1993, Gießen 1996); structure determination and refinement using the program SHELX-97 (G. M. Sheldrick, Göttingen 1997), scattering factors from International Tables, Vol. C (1992); $R_1(|F_o| > 4\sigma(F_o)) = 0.025$, $R_1(\text{all}) = 0.026$, $wR_2 = 0.054$, $GooF = 1.152$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-413183.

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