Crystal structure of hexapraseodymium dititanium septasulfide hexaoxide, $\text{Pr}_6\text{Ti}_2\text{S}_7\text{O}_6$

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Abstract

$\text{O}_6\text{Pr}_6\text{S}_7\text{Ti}_2$, monoclinic, $P12_1/m1$ (No. 11), $a = 11.944(2) \text{ \AA}$, $b = 3.9746(6) \text{ \AA}$, $c = 16.327(2) \text{ \AA}$, $\beta = 97.951(3)^\circ$, $V = 767.6 \text{ \AA}^3$, $Z = 2$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.086$, $T = 153 \text{ K}$.

Source of material

Single crystals of $\text{Pr}_6\text{Ti}_2\text{S}_7\text{O}_6$ were prepared from the reaction of Pr_2S_3 and TiO_2 in 2:1 ratio. KBr flux was employed to encourage crystal growth. The reactants were ground together and loaded into a fused silica tube that was then evacuated to approximately 10^{-4} Torr and sealed. The tube was heated to 1223 K over 24 hours, kept there for eight days, cooled at 1 K/h to 1123 K, kept there for four days, and then cooled at 3 K/h to room temperature. Black powder and lustrous red needles were obtained. The red crystals were found by EDS to contain Pr, Ti, and S in the approximate ratio 3:1:3. The closely related compound $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ was prepared previously [1] in an analogous manner from the reaction of La_2S_3 and TiO_2 . In that preparation the tube was cooled at 3 K/h directly from 1223 K to room temperature.

Discussion

There are no bonding interactions among S and O atoms in $\text{Pr}_6\text{Ti}_2\text{S}_7\text{O}_6$ so the compound may be described formally as containing Pr(III) and Ti(IV). The unit cells of $\text{Pr}_6\text{Ti}_2\text{S}_7\text{O}_6$ and $\text{La}_6\text{Ti}_2\text{S}_8\text{O}_5$ ($a = 12.572(10) \text{ \AA}$, $b = 4.053(2) \text{ \AA}$, $c = 16.289(14) \text{ \AA}$, $\beta = 96.79(1)^\circ$) [1] are similar and there are some close resemblances between the two structures. For example, in both structures the Ti1 and Ti2 atoms are in distorted octahedral environments. These octahedra form corner-sharing dimeric chains along [010] (see figure). However the bridging atom is an S atom in the present structure as opposed to an O atom in the La compound. The coordination environments of the Ti and Ln (Ln = Pr, La) atoms in the two structures are often different. In the La compound, the predominant geometry about the six independent La atoms is capped trigonal prismatic whereas in the present Pr structure it is square antiprismatic. Of course, given the different stoichiometries the distribution of O and S atoms in these coordination polyhedra differs between the two structures. Distances in $\text{Pr}_6\text{Ti}_2\text{S}_7\text{O}_6$ are consistent with those in other rare-earth oxysulfides: $d(\text{Pr}-\text{O}) = 2.337(5) \text{ \AA} - 2.955(14) \text{ \AA}$; $d(\text{Pr}-\text{S}) = 2.838(2) \text{ \AA} - 3.192(3) \text{ \AA}$; $d(\text{Ti}-\text{O}) = 1.780(11) \text{ \AA} - 2.021(2) \text{ \AA}$; $d(\text{Ti}-\text{S}) = 2.282(4) \text{ \AA} - 2.774(4) \text{ \AA}$.

Table 1. Data collection and handling.

Crystal:	red needle, size $0.012 \times 0.022 \times 0.160 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	205.93 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, $\Delta\omega = 0.3^\circ$
$2\theta_{\text{max}}$:	57.64°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4997, 2090
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1689
$N(\text{param})_{\text{refined}}$:	115
Program:	SHELXTL [2]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
O(1)	2e	0.2052(7)	1/4	0.7792(6)	0.012(2)
O(2)	2e	0.2750(9)	1/4	0.2231(7)	0.027(3)
O(3)	2e	0.3326(7)	1/4	0.3868(5)	0.010(2)
O(6)	2e	0.826(1)	1/4	0.6857(8)	0.045(3)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pr(1)	2e	0.02967(6)	1/4	0.62158(5)	0.0173(4)	0.0122(4)	0.0182(4)	0	0.0094(3)	0
Pr(2)	2e	0.06186(6)	1/4	0.89181(5)	0.0117(3)	0.0097(4)	0.0113(4)	0	0.0047(3)	0
Pr(3)	2e	0.40749(6)	1/4	0.88264(4)	0.0084(3)	0.0099(4)	0.0075(4)	0	0.0017(3)	0
Pr(4)	2e	0.47591(6)	1/4	0.28938(4)	0.0094(3)	0.0101(4)	0.0072(4)	0	0.0020(3)	0
Pr(5)	2e	0.67449(6)	1/4	0.52643(4)	0.0097(3)	0.0103(4)	0.0082(4)	0	0.0013(3)	0
Pr(6)	2e	0.71887(6)	1/4	0.87687(5)	0.0085(3)	0.0106(4)	0.0130(4)	0	−0.0008(3)	0
Ti(1)	2e	0.2042(2)	1/4	0.3121(2)	0.009(1)	0.079(3)	0.007(1)	0	0.002(1)	0
Ti(2)	2e	0.7766(2)	1/4	0.2346(2)	0.008(1)	0.045(2)	0.008(1)	0	0.0015(9)	0
S(1)	2e	0.0993(3)	1/4	0.0682(2)	0.008(1)	0.010(2)	0.012(2)	0	−0.001(1)	0
S(2)	2e	0.1146(3)	1/4	0.4601(2)	0.011(2)	0.017(2)	0.017(2)	0	0.003(1)	0
S(3)	2e	0.4212(2)	1/4	0.0603(2)	0.011(2)	0.012(2)	0.006(2)	0	0.003(1)	0
S(4)	2e	0.4484(3)	1/4	0.5814(2)	0.010(1)	0.013(2)	0.007(2)	0	0.003(1)	0
S(5)	2e	0.7689(2)	1/4	0.0717(2)	0.008(1)	0.011(2)	0.010(2)	0	−0.000(1)	0
S(6)	2e	0.7936(3)	1/4	0.3756(2)	0.012(2)	0.026(2)	0.008(2)	0	0.001(1)	0
S(7)	2e	0.9937(3)	1/4	0.2465(2)	0.007(2)	0.071(3)	0.011(2)	0	0.002(1)	0
O(4)	2e	0.5469(7)	1/4	0.7864(6)	0.014(4)	0.013(5)	0.006(5)	0	0.000(3)	0
O(5)	2e	0.6264(7)	1/4	0.2100(6)	0.011(4)	0.021(5)	0.010(5)	0	0.007(4)	0

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