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Crystal structure of ytterbium trisilicide, $YbSi_3$

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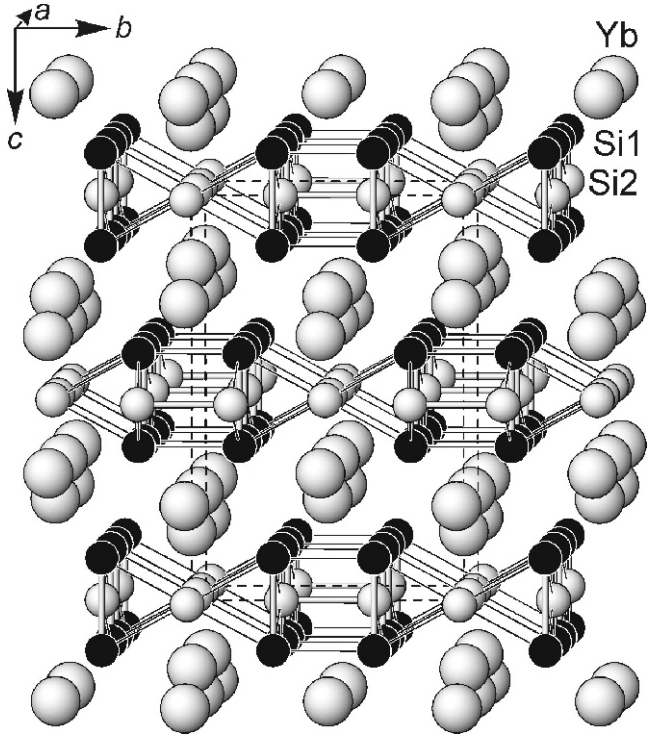

Abstract

Si_3Yb, tetragonal, *I*4/*mmm* (no. 139), a = 7.1657(2) Å, c = 10.6581(4) Å, V = 547.3 Å^3, Z = 8, $R_{gt}(F)$ = 0.020, $wR_{ref}(F^2)$ = 0.045, T = 293 K.

Source of material

Ytterbium trisilicide was prepared by arc melting of the rare-earth metal (Hunan Metal Company, 99.9 %, containing 270 ppm Ca and 180 ppm W) with silicon (Chempur, 99.999 %) followed by high-pressure high-temperature synthesis in a Walker-type module [1]. Reacting mixtures with an atomic ratio of 1:3 at 9.5(9) GPa and 1320(130) K using typical reaction times between 60 and 240 min yielded polycrystalline powders of $YbSi_3$. Single crystals were isolated from an ingot with a starting composition of 1:6 being compressed to 6.6(7) GPa and heated to 1770 K for 10 min before decreasing the temperature within 120 min to 1520 K at which the sample was kept for 60 min. Educt preparation, sample loading into and product isolation from the high-pressure equipment was performed in argon filled glove boxes (MBraun; H_2O, O_2 < 0.1 ppm).

Experimental details

In the advanced steps the refinement of the $YbSi_3$ structure model with two Yb and two Si positions resulted in the residuals $R1$ = 0.0204 and $wR2$ = 0.0445. The difference Fourier synthesis of this refinement evidenced a small peak (5.19 e·Å^3) at the 8*e* site (0, 0, 0.333), which is very close to the position of Yb1 (1.76 Å). In separate cycles we have included this position (Yb1a) to the refinement by using the scattering factor of Yb and constraining the occupancy with that of the Yb1 position. As a result of this procedure, the residuals dropped marginally to $R1$= 0.0196 and $wR2$ = 0.0442 resulting in occupancies of 0.991(2) and 0.009 for Yb1 and Yb1a, respectively. This finding is attributed to the presence of negligible disorder in the structure. For the final runs the ordered model of $YbSi_3$ was used (without the Yb1a position). Lattice parameters were refined from a powder diffraction pattern recorded with a Huber Guinier Imaging Plate Camera G670 (Cu Kα_1 radiation, λ = 1.54060 Å) by using the positions of 30 reflections and correcting with LaB_6 as internal standard (4.15692 Å). These parameter values were used for the interatomic distances calculation.

Discussion

The metastable high-pressure phase ytterbium trisilicide adopts a $CaSi_3$-type crystal structure which is characterized by two-dimensional silicon segments separated by twelve-coordinated rare-earth metal atoms. The layered Si arrangement comprises two types of dumbbells in orientations perpendicular and parallel to the crystallographic c axis, respectively. The Si—Si distances of 2.443(3) Å and 2.452(5) Å, respectively, in these dimeric units are compatible with covalent single bonds (2.351 Å) [2]. The diatomic fragments condense via four significantly longer Si—Si contacts (2.567(2) Å and 2.655(2) Å) into layers of interconnected cuboids. The shortest interlayer distance corresponds to 3.171 Å.

Table 1. Data collection and handling.

Crystal:	grey platelet, size 0.025 × 0.065 × 0.075 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	351.27 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, ω-oscillation
$2\theta_{max}$:	63.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2928, 306
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 300
$N(param)_{refined}$:	16
Programs:	SHELXL-97 [3], WinCSD [4]

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Yb(1)	8*e*	0	0	0.16973(5)	0.0078(2)	U_{11}	0.0074(2)	0	0	0
Yb(2)	8*d*	0	½	¼	0.0071(2)	U_{11}	0.0070(2)	0	0	0
Si(1)	2*m*	0.3147(2)	*x*	0.1146(2)	0.0089(4)	U_{11}	0.0102(7)	0.0015(6)	–0.0011(4)	U_{13}
Si(2)	4*i*	0.3289(3)	0	0	0.007(1)	0.0068(9)	0.0081(9)	0	0	0

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