Crystal structure of yttrium borosilicide, $Y_5Si_{2-x}B_8$ (x = 0.13)

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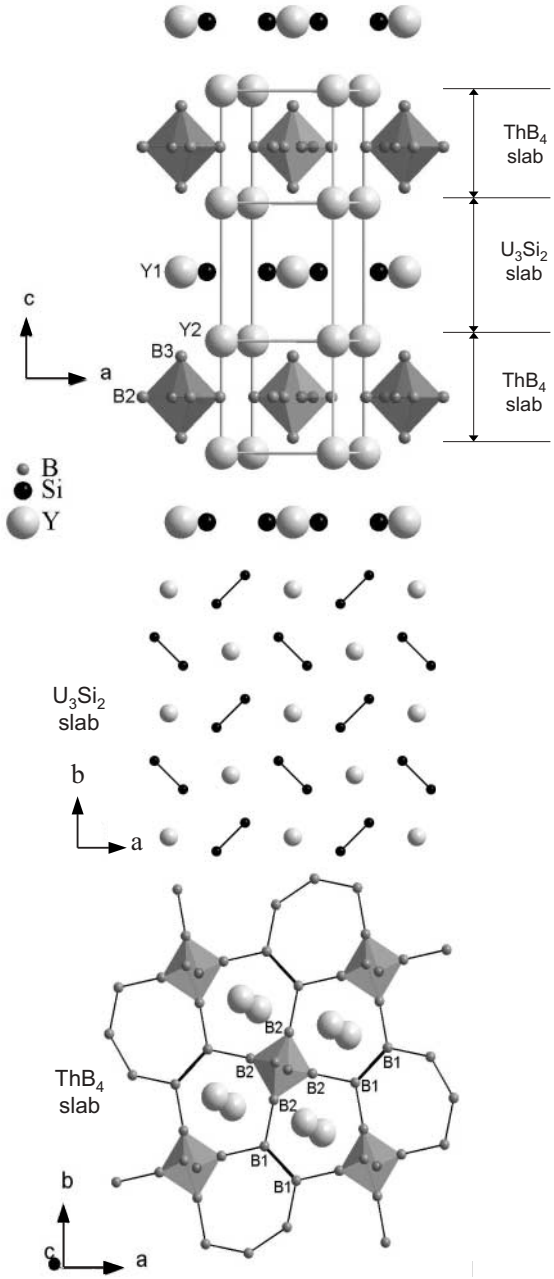

Abstract

$B_8Si_{1.87}Y_5$, tetragonal, *P4/mbm* (No. 127), a = 7.2234(2) Å, c = 8.0961(3) Å, V = 422.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.095, T = 293 K.

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Source of material

Suitable amounts of powder and freshly filed chips of the constituents in the nominal atomic percentage Y:Si:B=5:2:8 were mixed together and pressed into pellets. Samples melting was performed in an arc furnace using a non-consumable thoriated tungsten electrode under Ti/Zr-gettered argon atmosphere. To ensure homogeneity, the samples were turned over and re-melted several times. Shiny black platelet-like single crystals could be extracted from molten samples after crushing and used for structure determination.

Discussion

The ternary compound $Y_5Si_{2-x}B_8$ belongs to the family of rare earth borosilicides $R_5Si_2B_8$ (R = Sm, Gd, Tb, Dy), which we have recently discovered [1, 2]. This family of compounds crystallizes in the new structure type $Gd_5Si_2B_8$. The structure determination concludes to the occurrence of two yttrium (Y1, Y2) and three boron (B1, B2, B3) independent positions. On the other hand, there is only one silicon position, which has been found slightly deficient (τ = 0.935(9)). The structure $Y_5Si_2B_8$ can be easily described as an intergrowth structure of ThB_4 [3] and U_3Si_2 [4] related slabs of composition YB_4 and Y_3Si_2, following each other along the [001] direction (top figure). For example, the structure composition is confirmed by the resulting equation: $2YB_4 + Y_3Si_2 = Y_5Si_2B_8$. The salient characteristic of the structure results from the occurrence of two ordered independent boron and silicon sublattices. The silicon atoms within the U_3Si_2 related slab form Si—Si pairs with a Si—Si distance of 2.358(4) Å (middle figure). The boron atoms within the ThB_4 related slab form distorted B_6 octahedra, which are built from four B2 (square basis) and two B3 atoms. These octahedra, which are inserted in yttrium cubes, are close to ideal local O_h symmetry, as shown by the inter-octahedral B2—B3 and B2—B2 distances which are quite similar (1.81(1) Å and 1.84(1) Å, respectively; ave. 1.83(1) Å). The last boron atoms, namely the B1 atoms, lie in the same z = 1/2 as the B2 squares to which they are connected. Each B1 atom is connected to another B1 atom and to two B2 atoms which belong to two different octahedra, i.e. each B1 atom is three-coordinated (sp^2 hybridisation). The B1—B2 and B1—B1 distances of 1.76(1) Å and 1.82(2) Å, respectively, are slightly shorter than the intra-octahedron ones. As a result, the boron sublattice can be described as made of B_6 octahedra which are linked together in the (a, b) plane through boron atoms which form B—B pairs (bottom figure). It is worth noting that the B—B pairs (z = 1/2) are situated almost straight up the Si—Si ones (z = 0). Finally, the B1 and B2 atoms generate a two-dimensional planar (2-D) network which can be described as made of fused squares and heptagons (bottom figure). The Y1 atoms are octahedrally surrounded by two boron and four silicon atoms, while the Y2 ones are twelve-coordinated by nine boron and three silicon atoms, but in a more complex arrangement.

Table 1. Data collection and handling.

Crystal:	shiny black platelet, size 0.036 × 0.052 × 0.052 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	341.70 cm^{-1}
Diffractometer, scan mode:	Kappa CCD-Nonius, $\theta/2\theta$
$2\theta_{max}$:	69.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1730, 534
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 436
$N(param)_{refined}$:	28
Programs:	SIR97 [5], SHELXL-97 [6], DIAMOND [7]

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y(1)	2*a*		0	0	0	0.0136(3)	U_{11}	0.0057(4)	0	0	0
Y(2)	8*k*		0.81897(4)	–*x*+1/2	0.72410(6)	0.0077(2)	U_{11}	0.0069(3)	–0.0004(2)	0.0002(1)	$-U_{13}$
Si	4*g*	0.935(9)	0.3846(2)	–*x*+1/2	0	0.0112(8)	U_{11}	0.009(1)	0.0001(8)	0	0
B(1)	4*h*		0.9109(8)	*x*+1/2	1/2	0.012(2)	U_{11}	0.010(4)	0.005(3)	0	0
B(2)	8*j*		0.6724(7)	0.4597(8)	1/2	0.009(2)	0.010(2)	0.004(2)	–0.002(2)	0	0
B(3)	4*e*		0	0	0.337(1)	0.009(2)	U_{11}	0.010(3)	0	0	0

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