Journal of Solid State Chemistry **154,** 49–53 (2000)
doi:10.1006/jssc.2000.8810, available online at http://www.idealibrary.com on IDEAL®

Crystal Growth and Structure Analysis of a New Scandium Aluminum Boride Sc_2AlB_6

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Single crystals of a new ternary boride Sc_2AlB_6 were obtained from the Sc–Al–B system using high-temperature Al melts under an argon atmosphere. The growth conditions for large crystals were established. Sc_2AlB_6 crystals were obtained in the form of needle-like rectangles extending along the direction of the *b* axis or in the form of thick platelets with large *c* planes. The crystals were examined by powder X-ray diffraction and chemical analyses, and the crystal structure of Sc_2AlB_6 was investigated by single-crystal X-ray diffractometry. The crystal structure of Sc_2AlB_6 is of the Y_2ReB_6 type with the space group *Pbam* and the unit cell parameters are $a = 0.8937(3)$ nm, $b = 1.1226(3)$ nm, $c = 0.3433(1)$ nm, $V = 344.4(1) \times 10^{-3}$ nm^3, $Z = 4$. The structure refinement converged at an $R(F^2)$ value of 0.046 for 1545 reflections. The structural characteristics of Sc_2AlB_6 are discussed.

Key Words: **Sc_2AlB_6; crystal growth; structure analysis; Y_2ReB_6-type structure; orthorhombic structure.**

INTRODUCTION

Binary phase diagrams between rare earth element and boron have been understood as being well established (1). However, recently we found two new phases of REB_{25} (2) and REB_{50} (3) (RE = rare earth elements) for heavy rare earth elements. For the scandium–boron system the intermediate (ScB_2 (4), ScB_{12} (5)) phases and Sc-doped β-boron (6) have been reported. In the course of searching for new binary rare earth borides, we succeeded in synthesizing a new scandium boride, ScB_{19}, which has a tetragonal structure with $a = b = 1.02915(4)$ nm and $c = 1.42463(9)$ nm and is in the form of a crystalline powder, by the borothermal reduction method using Sc_2O_3 and amorphous B (7).

The simplest method for preparing single crystals of binary and ternary borides is growing them from high-temperature solutions in metallic melts (8–10). It may be possible to obtain ScB_{19} in the form of single crystals suitable for X-ray single-crystal diffraction analysis using Al flux. However, our attempts to do so were unsuccessful, but, instead of ScB_{19}, we obtained crystals of a new ternary scandium aluminum boride, Sc_2AlB_6, in addition to large crystals of ScB_2.

Previously synthesized RE_2AlB_6, which are expected to be isostructural to Y_2ReB_6 (11), are only Yb_2AlB_6 (12) and Lu_2AlB_6 (13). The orthorhombic crystal structure of the former was refined from powder X-ray diffraction data. We grew single crystals of the latter using the same Al flux method and measured microhardness, electrical resistivity, and oxidation behavior, but we determined only lattice parameters of the orthorhombic unit cell using powder X-ray diffraction data and have postponed single-crystal structure analysis up to now (13). Actually single-crystal structure analyses for RE_2AlB_6 have not yet been available.

In this work, we report on the synthesis conditions for growing crystals of Sc_2AlB_6. Furthermore, we describe the results of a structure refinement of Sc_2AlB_6 using single-crystal X-ray data.

EXPERIMENTAL DETAILS

Preparation and Phase Analyses

The starting materials were scandium oxide (Sc_2O_3 powder, purity 99.9%) or scandium metal (Sc chips, purity 99.9%), amorphous boron (B powder, purity 99.9%), and aluminum metal (Al chips, purity 99.99%). Boron and scandium oxide were weighed in the nominal composition (B/Sc = 6–22) (Table 1), and mixed with Al chips in a weight ratio of 1 : 15. The mixture of the starting materials was placed in a high-purity (99.9%) dense alumina crucible. The crucible was inserted into a vertical electric furnace with a SiC heater. Purified Ar gas flowed through in the furnace to protect against oxidation. The mixture of the starting materials was heated up to 1500°C at the rate of 300°C h^{-1}, kept there for 10 h, and then slowly cooled down at the rate of 50°C h^{-1}. After the temperature reached 1000°C, the furnace was rapidly cooled to room temperature. The crystals were separated from the solidified mixture by dissolving the excess Al with dilute hydrochloric acid for 5 days.

0022-4596/00 $35.00

TABLE 1
Growth Conditions of Sc–Al–B System Compounds

Run	Composition of the starting material (atomic ratio B : Sc)	Phase identified
1[a]	19 : 1	Sc–Al–B system, α-AlB_{12}, α-Al_2O_3
2[b]	6 : 1	ScB_2, α-Al_2O_3
3	8 : 1	ScB_2, α-Al_2O_3
4	10 : 1	ScB_2, α-Al_2O_3
5	12 : 1	ScB_2, α-Al_2O_3, Sc–Al–B system
6	14 : 1	Sc–Al–B system, α-Al_2O_3
7	16 : 1	Sc–Al–B system, α-Al_2O_3
8	18 : 1	Sc–Al–B system, α-Al_2O_3
9	20 : 1	Sc–Al–B system, α-Al_2O_3, α-AlB_{12}
10	22 : 1	Sc–Al–B system, α-Al_2O_3, α-AlB_{12}

[a] Scandium metal chips.

[b] The starting material for runs 2 to 10 was 2.0 g Sc_2O_3.

Experimental conditions for the growth of the single crystals are listed in Table 1.

X-Ray and Chemical Analyses

The morphological properties and impurities of the crystals were investigated by stereomicroscopy, scanning electron microscopy (SEM) (JEOL, JED-2140), and energy-dispersive X-ray analysis (EDX) (Horiba, EMAX-2770). The chemical composition was analyzed by electron probe microanalysis (EPMA) (JEOL, JXA8600MX) and inductively coupled plasma emission analysis (ICP) (Shimadzu, ICP-50).

The unit cell dimensions of Sc_2AlB_6 were determined from powder X-ray diffraction data (Rigaku, R-2000). Single-crystal structure analysis was carried out using a four-circle X-ray diffractometer (Rigaku, AFC-6) with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.071073$ nm).

RESULTS AND DISCUSSION

Syntheses of Sc_2AlB_6

Typical experimental conditions for the growth of Sc_2AlB_6 crystals are listed in Table 1. The atomic ratio B/Sc in the starting mixture was varied from 6 to 22 (runs 1 to 10).

TABLE 2
Chemical Analysis Data of Sc–Al–B Compounds

Phase	Crystal	Chemical analysis (wt%)				Chemical composition
		Sc	Al	B	In total	
Sc–Al–B	Needle	49.45	11.74	38.64	99.83	$Sc_{1.85}Al_{0.73}B_6$
Sc–Al–B	Plate	47.98	12.68	39.91	100.57	$Sc_{1.73}Al_{0.76}B_6$

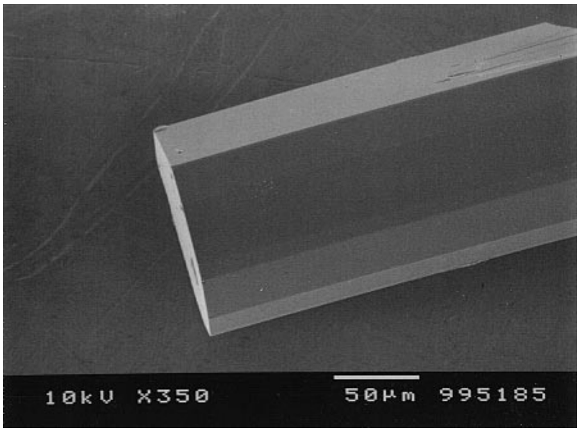

FIG. 1. SEM photograph of a Sc_2AlB_6 crystal (run 1).

As seen in Table 1, ScB_2, a ternary Sc–Al–B compound, α-AlB_{12}, and α-Al_2O_3 were obtained, while crystals of ScB_{12} and ScB_{19} were not detected by powder X-ray diffraction. Powder X-ray diffraction intensities of the Sc–Al–B compound could be indexed by an orthorhombic unit cell with lattice constants $a = 0.8937(3)$ nm, $b = 1.1226(3)$ nm, $c = 0.3433(1)$ nm, and $V = 344.4(1) \times 10^{-3}$ nm^3. According

TABLE 3
Crystallographic and Data Collection Data of Sc_2AlB_6

Crystal system	Orthorhombic
Space group	*Pbam* (No. 55)
a (nm)	0.8937(3)[a]
b (nm)	1.1226(3)[a]
c (nm)	0.3433(1)[a]
Volume (nm^3)	$344.4(1) \times 10^{-3}$
Z	4
fw	181.75
D_x (g/cm^3)	3.505
Applied radiation, λ (nm)	Monochromatic Mo$K\alpha$ 0.071073
Linear absorption coefficient μ (mm^{-1})	3.96
Crystal dimensions (mm)	$0.25 \times 0.075 \times 0.075$
Absorption correction	Empirical (Ψ scans)
Data corrections	Lorentz, polarization
Reflections measured	$-17 \leqq h \leqq 17$ $0 \leqq k \leqq 22$ $0 \leqq l \leqq 6$
$2\theta_{max}$ (degrees)	90.35
Unique reflections	1545
Structure refinement program	SHELX97 (based on F_o^2)
Number of variables	41
$R1^b[F_o > 4\sigma(F_o)]$ (for 1349F_o)	0.037
$R1$ [all F_o] (for 1545F_o)	0.046
WR2 $(F^2)^b$	0.089

[a] The lattice constants were obtained from powder XRD.

[b] $R1 = \sum \|F_o| - |F_o\| / \sum |F_o|$; $WR2 = [\sum |w(F_o^2 - F_c^2)^2| / \sum |w(F_o^2)^2|]^{1/2}$; $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

TABLE 4
Boron Coordinates and Isotropic Displacement Parameters in Sc_2AlB_6

Atom[a]	Site	x/a	y/b	z/c	$U(\times 10^{-5}, nm^2)$
B1	4h	0.0516(2)	0.0631(2)	$\frac{1}{2}$	7.1(3)
B2	4h	0.2534(2)	0.0782(2)	$\frac{1}{2}$	7.0(3)
B3	4h	0.2978(3)	0.2384(2)	$\frac{1}{2}$	6.7(3)
B4	4h	0.1306(2)	0.3195(2)	$\frac{1}{2}$	7.0(3)
B5	4h	0.4782(2)	0.2885(2)	$\frac{1}{2}$	6.9(3)
B6	4h	0.0995(2)	0.4727(2)	$\frac{1}{2}$	5.7(3)

[a] No deviation from full occupancy; thermal factor $T = \exp(-8\pi^2 U[\sin(\theta)]^2)$.

to the chemical compositions shown in Table 2 and similarity of unit cell parameters with Yb_2AlB_6 and Lu_2AlB_6 we assigned the Sc–Al–B compound as an isostructural compound Sc_2AlB_6. Variation of the atomic ratio of the starting materials gave different products. With increased boron concentration, more boron-rich phases were formed. The optimum conditions for growing Sc_2AlB_6 were established using a starting mixture of B/Sc = 19. On the other hand, the relative intensity of the reflections of ScB_2 in the X-ray patterns became remarkably large for B/Sc = 8. Sc_2AlB_6 crystals were obtained in the form of needle-like rectangles extending in the *b* axis direction (Fig. 1) or thick platelets with large *c* planes. The largest Sc_2AlB_6 crystals had maximum dimensions of about $0.2 \times 0.2 \times 3.5$ mm^3. Sc_2AlB_6 crystals had a silver color and metallic luster.

Structure Investigations and Discussion of the Sc_2AlB_6 Structure

In our study we investigated three crystals of Al flux-grown Sc_2AlB_6. The reciprocal lattice of all of them could be easily indexed on the basis of *Pbam* space group symmetry. Weissenberg photographs of the oriented crystals gave no indication of a superstructure formation. Nevertheless two of them showed a very few (5 of 1572 and 3 of 1540 independent reflexes) systematic absence violations while the third one showed none. An atomic arrangement isotypic to the Y_2ReB_6-type of structure (11) could be refined for all three of them. The refinement presented here is based on the data set that showed no absence violations since the very small number of additional reflexes in the other two sets were not sufficient to draw any kind of conclusion about possible structural changes.

TABLE 6
Selected Interatomic Distances for Metal Atoms in Sc_2AlB_6

Central atom	Ligand	Distance $(\times 10^{-1}$, nm)	Central atom	Ligand	Distance $(\times 10^{-1}$, nm)
Sc1	2B2	2.607(2)	Sc2	2B4	2.464(2)
	2B3	2.617(2)		2B6	2.479(2)
	2B5	2.629(2)		2B2	2.482(2)
	2B6	2.633(2)		2B6	2.483(2)
	2B1	2.665(2)		2B3	2.486(2)
	2B4	2.698(2)		2B5	2.504(2)
	2B1	2.700(2)		Al	2.770(1)
	1Al	3.012(2)		Al	2.780(1)
	1Al	3.072(1)		Sc2	3.051(1)
Al	2B5	2.277(2)			
	2B2	2.294(2)			
	2B1	2.299(2)			
	2B3	2.311(2)			
	2B4	2.325(2)			
	Sc2	2.770(2)			
	Sc2	2.780(1)			
	Sc1	3.012(2)			
	Sc1	3.052(2)			
	Sc1	3.072(1)			

The crystal structure of Sc_2AlB_6 was refined using the SHELX97 program package (14). Crystallographic details are given in Table 3. The structure refinement was based on 1545 intensity values in the 2θ range 5.0°–90.35°. The proposed atomic coordinates for Y_2ReB_6 (11) were used as initial parameters for the least-squares refinement of the coordinates of Sc_2AlB_6. A total of 41 parameters were refined. The final Bragg *R* value, unweighed *R* value, and weighed *R* value were 0.037, 0.046, and 0.089, respectively. The coordinates of the B atoms and their isotropic displacement parameters are given in Table 4. The metal

TABLE 5
Metal Coordinates and Anisotropic Displacement Parameters in Sc_2AlB_6[a]

Atom	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sc1	4*g*	0.82017(4)	0.08649(3)	0.0	5.4(1)	4.6(1)	7.4(1)	0	0	− 0.2(1)
Sc2	4*g*	0.44388(4)	0.12831(2)	0.0	6.2(1)	4.7(1)	5.8(1)	0	0	0.3(1)
Al	4*g*	0.14085(8)	0.18003(6)	0.0	4.5(2)	4.9(3)	11.2(3)	0	0	0.3(1)

[a] Sc1, Sc2 sites fully occupied; Al site refines to 90(1)% occupation.

$U_{ij}(\times 10^{-5}, nm^2)$; thermal factor $T = \exp(-2\pi^2[h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \cdots + 2hka^*b^*U_{12}])$ isotropic U_{eq} (one-third of the trace of the orthogonalized U_{ij} tensor).

TABLE 7
Selected Interatomic Boron–Boron Distances in Sc_2AlB_6

Central atom	Ligand	Distance ($\times 10^{-1}$, nm)	Central atom	Ligand	Distance ($\times 10^{-1}$, nm)
B1	B1	1.702(4)	B4	B6	1.743(3)
	B5	1.785(3)		B3	1.750(3)
	B2	1.811(3)		B5	1.823(3)
B2	B6	1.770(3)	B5	B3	1.708(3)
	B1	1.811(3)		B1	1.785(3)
	B3	1.841(3)		B4	1.823(3)
B3	B5	1.708(3)	B6	B4	1.743(3)
	B4	1.750(3)		B2	1.770(3)
	B2	1.841(3)		B6	1.883(4)

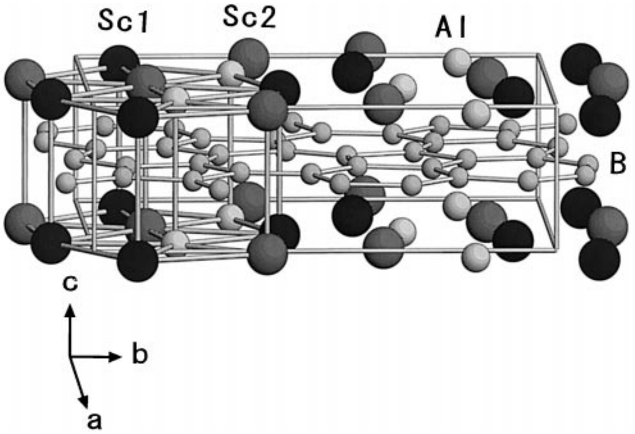

FIG. 3. Crystal structure of Sc_2AlB_6: three-dimensional view.

coordinates and isotropic displacement parameters for the Sc atoms are given in Table 5. Selected interatomic distances are given in Tables 6 and 7.

Sc_2AlB_6 is the first representative of the Y_2ReB_6 structure family for which the structure has been determined by single-crystal X-ray diffractometry. The crystal structure of Sc_2AlB_6 is illustrated in Figs. 2 and 3. The Y_2ReB_6 structure is characterized by a two-dimensional boron network (composed of 5-, 6-, and 7-membered rings) sandwiched between metal layers. These boron atoms reside in the interstitial sites of trigonal prisms formed by the Sc and Al atoms. Similar boron and metal layer arrangements are observed in the orthorhombic (space group: *Pbam*) $YCrB_4$ (15) structure type. There boron atoms (trigonal prismatically coordinated by the metal atoms) form 5- and 7-membered rings. Based on this boron-ring formation tendency the three structure types $YCrB_4$, Y_2ReB_6, and AlB_2 are closely related. In hexagonal AlB_2 and ScB_2 boron atoms form 6-membered rings. Nevertheless under the experimental conditions reported here no formation of a "$ScAlB_4$" phase could be observed. In fact crystal platelets of ScB_2 were found to be the only by-product in these experiments.

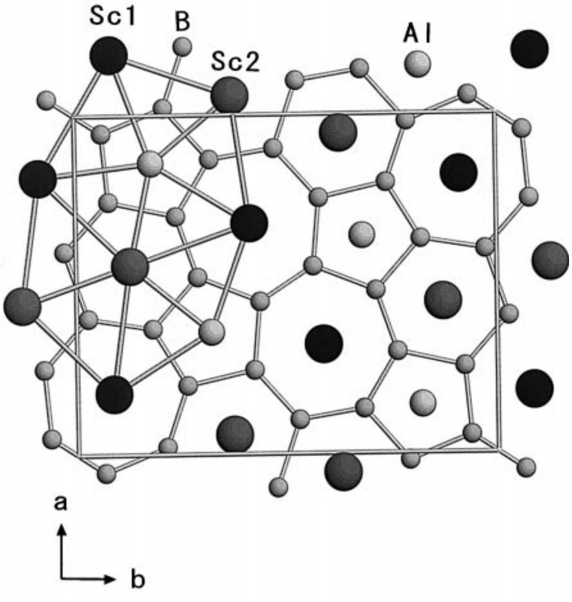

FIG. 2. Crystal structure of Sc_2AlB_6: projection along the *c* axis.

Refinement of the Sc_2AlB_6 crystal structure resulted in a slightly substoichiometric occupation (90(1)%) of the Al position together with a pronounced anisotropic thermal vibration behavior. In the Al coordination polyhedron Al is bonded more strongly to the neighboring Sc atoms ($\approx 0.277 < d_{\mathrm{Sc1,\ 2Al}} < 0.307$ nm) than to the B1–B5 atoms forming 5-membered rings ($\approx 0.228 < d_{\mathrm{AlB}} < 0.233$ nm). The distances observed in the metal layer are substantially shorter than the sums of the corresponding atomic radii ($2r_{\mathrm{Sc}} = 0.324$ and $r_{\mathrm{Sc}} + r_{\mathrm{Al}} = 0.305$ nm). Distances between metal and boron atoms show no significant contractions. In layered AlB_2 interatomic distances $d_{\mathrm{AlB}} \approx 0.238$ nm (16) and in ScB_2 $d_{\mathrm{ScB}} \approx 0.253$ nm can be found. Therefore the thermal motion of Al in Sc_2AlB_6 is expected to be larger in the plane perpendicular to the metal sheets. In fact a small residual electron density could be found above and below the Al positions, indicating the possible occurrence of local

TABLE 8
Unit Cell Parameters of the Y_2ReB_6-Type Structure Compounds

	Unit cell parameter (nm)				
Phases	*a*	*b*	*c*	$V (\times 10^{-3}, \mathrm{nm}^3)$	Ref.
Y_2ReB_6	0.9175	1.155	0.3673	389.2	(11)
Yb_2AlB_6	0.9127(5)	1.146(1)	0.3584(4)	374.9(1)	(12)
Lu_2AlB_6	0.8987(1)	1.1334(1)	0.3633(1)	370.1(1)	(13)
Sc_2AlB_6	0.8937(3)	1.1226(3)	0.3433(1)	344.4(1)	This work

disorder manifested by the "rattling" and partial occupation by Al. Up to now Yb_2AlB_6 (12), Lu_2AlB_6 (13) (crystal structure refined from powder data), and Sc_2AlB_6 are the only three examples of compounds adopting the Y_2ReB_6-type of structure which could be grown from an Al flux and are listed in Table 8. The unit cell parameters of Sc_2AlB_6 are smaller than those of Yb_2AlB_6 and Lu_2AlB_6, which is expected because of the smaller atomic radius of scandium in comparison with that of ytterbium and lutetium.

CONCLUSION

The single crystals of a new ternary boride Sc_2AlB_6 have been grown from high-temperature aluminum flux using scandium metal or scandium oxide and amorphous boron powders as starting materials under an argon atmosphere. Growth conditions for large crystals were established. Sc_2AlB_6 is the first compound obtained in the ternary system Sc–Al–B.

The crystals were examined by powder X-ray diffraction and chemical analyses and single-crystal X-ray diffractometry. Sc_2AlB_6 is the first representative of the Y_2ReB_6 structure family the structure of which has been determined by single-crystal X-ray diffractometry.

Since crystal growth from metal fluxes is a very versatile method allowing variation of numerous experimental parameters (e.g., temperature profiles, metal fluxes, and composition ratios) most likely compounds containing Al and the heavy rare earth metals Gd–Yb could be synthesized in a similar way.

ACKNOWLEDGMENTS

The authors thank Dr. K. Kudou of Kanagawa University and Dr. K. Iizumi of Tokyo Institute of Polytechnics for help in the experiments.

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