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# Growth and some properties of $Sc_2AlB_6$ crystal obtained from the solution in aluminum melt

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**Abstract**

Crystals of $Sc_2AlB_6$ were grown using scandium oxide and elemental boron as starting materials in a self-component aluminum solution under an argon atmosphere. The growth conditions for obtaining single crystals of relatively large size were investigated. $Sc_2AlB_6$ single crystals were obtained in the form of prisms extending in the *b*-axis direction. The largest $Sc_2AlB_6$ crystals prepared had maximum dimensions of about $0.4 \times 0.4 \times 4.2\,mm^3$. The values of the Vickers microhardness and the electrical resistivity of $Sc_2AlB_6$ crystals are $12.7 \pm 0.8$ GPa and $43 \pm 8\,\mu\Omega\,cm$, respectively. The oxidation of $Sc_2AlB_6$ crystals starts at about 773°C, and the weight gain after TG determination is 12.9 mass% at 1200°C. The oxidation products of $Sc_2AlB_6$ crystals could not determined.


*Keywords:* $Sc_2AlB_6$; Solution in aluminum melt; Vickers microhardness; Electrical resistivity; Oxidation resistance

## 1. Introduction

In most of the known ternary rare earth borides, three types of ternary structures have been reported, namely the $YCrB_4$-type (S.G.: *Pbam*), $Y_2ReB_6$-type (S.G.: *Pbam*) and $REAlB_{14}$-type (*RE* = rare earth element) (S.G.: *Imma*) [1–3]. The $Lu_2AlB_6$ phase crystallizing in the $Y_2ReB_6$-type structure displays relatively high thermal stability and high hardness [4]. The present authors are interested in chemical and physical properties of $Y_2ReB_6$-type compounds of ternary rare earth borides. However, the data available on the properties for compounds *iso*-structural to the $Y_2ReB_6$-type are very scarce. In our previous work, we succeeded to synthesize a new ternary boride, $Sc_2AlB_6$. The crystals were obtained from a self-component aluminum solution using scandium metal and boron elements as starting materials. The crystal structure was determined by single-crystal X-ray diffractometry [5]. As shown in Fig. 1, the $Sc_2AlB_6$ structure is built up 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. However, we did not carry out any measurements of chemical and physical properties of the $Sc_2AlB_6$ crystals obtained.

In the present work, we report the experimental conditions for growing $Sc_2AlB_6$ crystals of relatively large size, using scandium oxide and elemental boron in a self-component aluminum solution under an argon atmosphere. In addition, measurements of Vickers microhardness and electrical resistivity for the as-grown $Sc_2AlB_6$ crystals were carried out, and oxidation resistance was investigated at high temperature in air.

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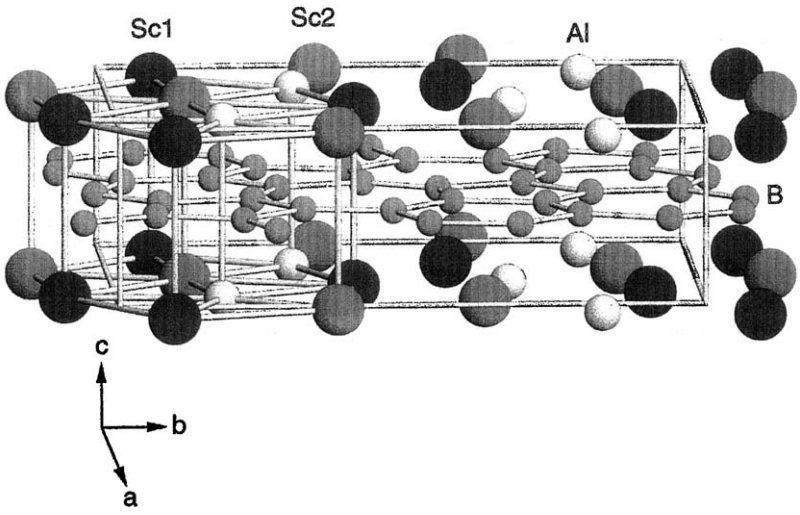


Fig. 1. Crystal structure of $Sc_2AlB_6$: three-dimensional view. Large gray, large open and small gray circles represent Sc, Al and B atoms, respectively.

## 2. Experimental

The $Sc_2AlB_6$ crystals were prepared from scandium oxide powder (99.9% purity), amorphous boron (99.9% purity) and aluminum chips (99.99% purity). $Sc_2O_3$ and B powders were weighed in with atomic ratios $n = B/Sc = 5-25$ (Table 1) according to the reaction

$$Sc_2O_3 + (2n+3)B \rightarrow 2ScB_n + 3BO. \quad (1)$$

Al metal was added to each mixture at a mass ratio of 1:15. The mixture of starting materials was placed in a high-purity alumina (99.9% purity) crucible and heated under an argon gas. The temperature of the furnace was raised at a rate of $300^\circ C\,h^{-1}$ up to 1500°C and held for 10 h at that temperature, and then slowly cooled down at a rare of $50^\circ C\,h^{-1}$ to 1000°C. Subsequently the furnace was rapidly cooled down to room temperature. The crystals were removed from the solidified melt by dissolving the matrix in about $6\,mol\,dm^{-3}$ hydrochloric acid.

Relatively large single crystals of $Sc_2AlB_6$ were selected under a stereomicroscope for chemical analyses and measurements Vickers microhardness, electrical resistivity and oxidation resistance. The morphological properties and impurities of the crystals were investigated by a scanning electron microscope (SEM) (JEOL, JED-2140) and an energy dispersive X-ray detector (EDX)(Horiba, EMAX-2770). The chemical composition was determined by an electron probe microanalyser (EPMA) (JEOL, JXA8600MX) and an inductively coupled plasma emission analyser (ICP) (Shimadzu, ICP-50). The crystalline phases were determined using powder X-ray diffraction data (XRD) (Rigaku, R-2000) with monochromatic Cu$K\alpha$ radiation. The unit-cell parameters of $Sc_2AlB_6$ were determined using a Guinier–Hägg focusing X-ray powder diffraction camera [6] with monochromatic Cu$K\alpha_1$ radiation and silicon as internal calibration standard. The density of the crystals was measured using a pycnometer with distilled water at room temperature. The X-ray density was determined using the result of the measurements of the unit-cell parameters.

Table 1
Synthesis conditions of $Sc_2AlB_6$ crystals from solution in aluminum melt

| Run no. | Composition of the starting material (atomic ratio Sc:B) | Phases identified |
|---|---|---|
| 1 | 1:5 | $ScB_2$, $\alpha$-$Al_2O_3$ |
| 2 | 1:6 | $ScB_2$, $\alpha$-$Al_2O_3$ |
| 3 | 1:8 | $ScB_2$, $\alpha$-$Al_2O_3$ |
| 4 | 1:10 | $ScB_2$, $\alpha$-$Al_2O_3$ |
| 5 | 1:12 | $ScB_2$, $\alpha$-$Al_2O_3$, $Sc_2AlB_6$ |
| 6 | 1:14 | $Sc_2AlB_6$, $\alpha$-$Al_2O_3$ |
| 7 | 1:16 | $Sc_2AlB_6$, $\alpha$-$Al_2O_3$ |
| 8 | 1:18 | $Sc_2AlB_6$, $\alpha$-$Al_2O_3$ |
| 9 | 1:20 | $Sc_2AlB_6$, $\alpha$-$Al_2O_3$, $\alpha$-$AlB_{12}$ |
| 10 | 1:22 | $Sc_2AlB_6$, $\alpha$-$Al_2O_3$, $\alpha$-$AlB_{12}$ |
| 11 | 1:24 | $\alpha$-$AlB_{12}$, $\alpha$-$Al_2O_3$ |
| 12 | 1:25 | $\alpha$-$AlB_{12}$, $\alpha$-$Al_2O_3$ |

Al metal was added to each mixture at a mass ratio of 1:15.
The starting materials were soaked at 1500°C for 10 h.

The microhardness of the as-grown $Sc_2AlB_6$ crystals was measured using a Vickers diamond indenter [7,8] at room temperature. A load of 0.98 N was applied for 15 s at about 7 positions on a well-developed (010) face of the crystal. The electrical resistivity value of as-grown $Sc_2AlB_6$ crystals was measured by a direct-current four-probe technique [9] at room temperature in air. The values of hardness and electrical resistivity were averaged and the experimental error was estimated. The oxidation resistance of $Sc_2AlB_6$ was studied by TG-DTA [7,10] analyses, when the samples were heated in air at a rate of $10^\circ C\,min^{-1}$ up to 1200°C.

## 3. Results and discussion

### 3.1. Growth of $Sc_2AlB_6$ crystals

The results of the phase analysis are listed in Table 1. As seen from Table 1, $Sc_2AlB_6$, $ScB_2$, α-$AlB_{12}$ and α-$Al_2O_3$ were formed. The variation of the atomic ratio of the starting materials gave different compounds, and with increased boron concentration, more boron-rich aluminum borides were obtained. The $Sc_2AlB_6$ phase became strongly dominating in the range of atomic ratios B/Sc = 14−18 (Run no. 6–8). It is believed that the major part of α-$Al_2O_3$ came from minute fragments of the alumina crucible sticking to the crystals and from an $Al_2O_3$ mortar, which was used to pulverize the crystals. $Sc_2AlB_6$ single crystals, having silver color and metallic lustre, were generally obtained in the form of prisms extending in the *b*-axis direction (Fig. 2). The largest $Sc_2AlB_6$ crystals prepared had the maximum dimensions of about $0.4 \times 0.4 \times 4.2\,mm^3$. The basic crystal data, unit-cell parameters, density and chemical composition of as-grown $Sc_2AlB_6$ are listed in Table 2. The unit-cell parameters of $Sc_2AlB_6$ (Table 2) are smaller than those of $Yb_2AlB_6$ [11] and $Lu_2AlB_6$ [4], with the following values for $Yb_2AlB_6$ $a = 0.9127(5)$ nm, $b = 1.146(1)$ nm, $c = 0.3584(4)$ nm, $V = 374.9(1) \times 10^{-3}$ nm$^3$; and for $Lu_2AlB_6$ $a = 0.8987(1)$ nm, $b = 1.1334(1)$ nm, $c = 0.3633(1)$ nm, $V = 370.1(1) \times 10^{-3}$ nm$^3$, respectively. The values of the unit-cell volume $V$ decreases with decreasing atomic size of *RE* in $RE_2AlB_6$ (*RE* = Sc, Yb, Lu). The measured density is close to the X-ray density. The impurity content of $Sc_2AlB_6$ crystals was not analyzed chemically. However, no evidence has been obtained for the presence of an oxygen-containing phase in the crystals, as concluded from EDX and EPMA of as-grown crystals.

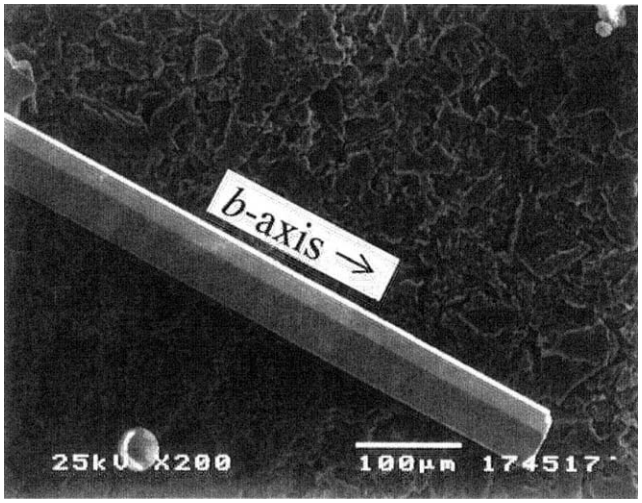


Fig. 2. SEM photograph of a $Sc_2AlB_6$ single crystal (Run no. 6).

Table 2
Crystal data and chemical analysis data of $Sc_2AlB_6$ crystal

| | |
|---|---|
| Formula unit | $Sc_2AlB_6$ |
| Run no. | 6 |
| Crystal | Prismatic shape |
| Crystal system | Orthorhombic |
| Space group | *Pbam* (No. 55) |
| *a* (nm) | 0.8936(2) |
| *b* (nm) | 1.1228(3) |
| *c* (nm) | 0.3432(1) |
| *V* (nm$^3$) | $344.3(1) \times 10^{-3}$ |
| *Z* | 4 |
| $D_x$ (g cm$^{-3}$) | 3.305 |
| $D_m$ (g cm$^{-3}$) | 3.28(2) |
| Sc (mass%) | 48.7 |
| Al (mass%) | 12.2 |
| B (mass%) | 39.3 |
| In total | 100.2 |
| Chemical composition | $Sc_{1.8}Al_{0.7}B_6$ |

### 3.2. Properties

The Vickers microhardness of as-grown $Sc_2AlB_6$ crystals was measured in several directions on the (010) faces. The hardness value is listed in Table 3 together with previously published data for $Lu_2AlB_6$ [4]. The values measured on (010) faces of $Sc_2AlB_6$ crystals are slightly lower than that observed of $18.9 \pm 0.7$ GPa for $Lu_2AlB_6$ in the literature. It seems to be that the microhardness changes having metal elements content in the boron networks built up by five-, six-, and seven-membered rings. Considering the difference for metal elements in the structure, especially between $Sc_2AlB_6$ and $Lu_2AlB_6$, the difference in the microhardness of their compounds is noteworthy.

The electrical resistivity of as-grown crystals was measured parallel to the *b*-axis for $Sc_2AlB_6$. The electrical resistivity values are listed in Table 3 together with previously published data for $Lu_2AlB_6$ [4]. The electrical resistivity values of $Sc_2AlB_6$ crystals were found to be closely similar to the values of $Lu_2AlB_6$ crystals.

The oxidation process of $Sc_2AlB_6$ crystals was studied at temperature below 1200°C by TG-DTA analyses. The results are presented together with previously published data for $Lu_2AlB_6$ [4] in Fig. 3. The oxidation of $Sc_2AlB_6$ starts at about 773°C, and the oxidation reaction of $Lu_2AlB_6$ began to proceed at about 1030°C. $Sc_2AlB_6$ shows low oxidation resistance, while $Lu_2AlB_6$ shows relatively high oxidation resistance. The resistance towards oxidation seems to be related to thermodynamic stability. The weight gain of $Sc_2AlB_6$ after TG determination is 12.9 mass% at 1200°C. $Sc_2AlB_6$ crystal did not exhibit any endothermic or exothermic peaks in the DTA curve. The final oxidation products of the crystal were not detected from XRD, probably due to insufficient amount of the oxidation product.

Table 3
Vickers microhardness and electrical resistivity of $RE_2AlB_6$ ($RE$ = Sc, Lu) crystals

| Compound | Hardness (GPa) | Electrical resistivity (μΩ cm) | Reference |
|---|---|---|---|
| $Sc_2AlB_6$ | $12.7 \pm 0.8$ | $43 \pm 8$ | This work |
| $Lu_2AlB_6$ | $18.9 \pm 0.7$ | $31 \pm 3$ | [4] |

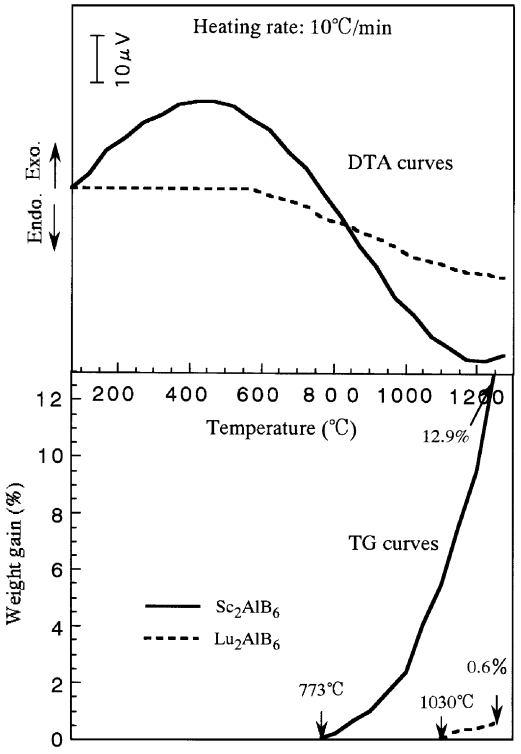


Fig. 3. TG-DTA curves of $Sc_2AlB_6$ and $Lu_2AlB_6$ crystals heated in air.

## 4. Conclusion

The single crystals of $Sc_2AlB_6$ were grown using scandium oxide and element boron as starting materials in a self-component aluminum solution under an argon atmosphere. $Sc_2AlB_6$ single crystals, having silver color and metallic lustre, were generally obtained in the form of prisms extending in the $b$-axis direction. The largest $Sc_2AlB_6$ crystals prepared had the maximum dimensions of about $0.4 \times 0.4 \times 4.2\,mm^3$. $Sc_2AlB_6$ belongs to the orthorhombic system and crystallizes in the $Y_2ReB_6$-type structure: space group *Pbam* (No. 55), $a = 0.8936(2)$ nm, $b = 1.1228(3)$ nm, $c = 0.3432(1)$ nm, $V = 344.3(1) \times 10^{-3}\,nm^3$. The present study of $Sc_2AlB_6$ single crystals is the first physical and chemical properties study. The values of the Vickers microhardness and electrical resistivity of $Sc_2AlB_6$ crystals are $12.7 \pm 0.8$ GPa and $43 \pm 8$ μΩ cm, respectively. The oxidation of $Sc_2AlB_6$ crystals starts at about 773°C. Weight gain of the $Sc_2AlB_6$ after TG determination are 12.9 mass%. The oxidation products of $Sc_2AlB_6$ crystals could not determined.

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