Original Paper

Growth and Some Properties of $REAlB_4$ and RE_2AlB_6 (RE = Rare Earth Element) Crystals

Shigeru OKADA[1,*], Toetsu SHISHIDO[2], Takao MORI[3], Kunio KUDOU[4], Kiyokata IIZUMI[5], Kazuo NAKAJIMA[2]

[1]Faculty of Science and Engineering, Kokushikan University, 4-28-1 Setagaya, Setagaya-ku, Tokyo 154-8515
[2]Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577
[3]National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044
[4]Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686
[5]Faculty of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi 243-0297

Received October 6, 2007; E-mail: sokada@kokushikan.ac.jp

Single crystals of $TmAlB_4$, $YbAlB_4$, $LuAlB_4$ and Lu_2AlB_6 were grown using RE_2O_3 (RE = Tm, Yb, Lu) and crystalline boron as starting materials in a self-component aluminum solution under an argon atmosphere at 1773 K for 10 h. $REAlB_4$ (RE = Tm, Yb, Lu) ($YCrB_4$-type, orthorhombic, space group *Pbam*) and Lu_2AlB_6 (Y_2ReB_6-type, orthorhombic, space group *Pbam*) crystals were generally obtained in the form of a prismatic shape extending in the *c* direction and with well developed {001} or {100} faces. $REAlB_4$ and Lu_2AlB_4 crystals had a maximum size of approximately 3.5 mm. The Vickers microhardness values at room temperature for $REAlB_4$ and Lu_2AlB_6 in several directions on {001} and {100} planes were from 14 to 15 (±1) and 19 (±1) GPa, respectively. The magnetic susceptibility of $REAlB_4$ (RE = Yb, Lu) and Lu_2AlB_6 increases paramagnetically as temperature is lowered, an effect in which we attribute to impurities. Superconductivity was not observed in any of the samples down to a temperature of 2 K. An anti-ferromagnetic transition with a Neel transition temperature of T_N = 5.5 K was found in $TmAlB_4$.

Key Words: *$REAlB_4$ (RE = Rare Earth Element)*, *Lu_2AlB_6*, *Crystallographic Data*, *Hardness*, *Magnetic Properties*

1. Introduction

Three types of ternary compounds have been reported in RE-Al-B (RE = Tm, Yb, Lu) systems, namely RE_2AlB_6 (Y_2ReB_6-type, orthorhombic, space group *Pbam*), $REAlB_4$ ($YCrB_4$-type, orthorhombic, space group *Pbam*) and $REAlB_{14}$ ($MgAlB_{14}$-type, orthorhombic, space group *Imma*) [1-7]. RE_2AlB_6 and $REAlB_4$ crystals are of great interest because of their remarkable physical and chemical properties, which are of potential interest in as thermoelectric and photodetector materials [8]. However, there is very little information about the physical and chemical properties of $REAlB_4$ and RE_2AlB_6 crystals. $REAlB_4$ has the same structure as that postulated for $YCrB_4$ (Fig.1). The Lu_2AlB_6 structure is shown in Fig.2. The structural features of Lu_2AlB_6 are conveniently discussed together with those of the $YCrB_4$ structure and its structure block shifted variant, the $ThMoB_4$ structure [9] with orthorhombic symmetry (space group *Cmmm*). The linkage of boron atoms in the structures of $YCrB_4$-type and Lu_2AlB_6 (Y_2ReB_6-type) differs according to the chemical composition as follows: in $REAlB_4$, the boron network is built up by five- and seven-membered rings, while in RE_2AlB_6, the boron network consists of five-, six-, and seven-membered rings. The structures of $REAlB_4$ and RE_2AlB_6 are built up by two-dimensional boron networks sandwiched between metal layers. These boron atoms

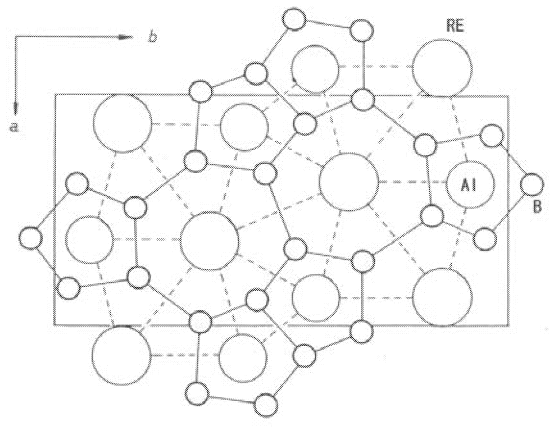

Fig.1 The crystal structure of $REAlB_4$.

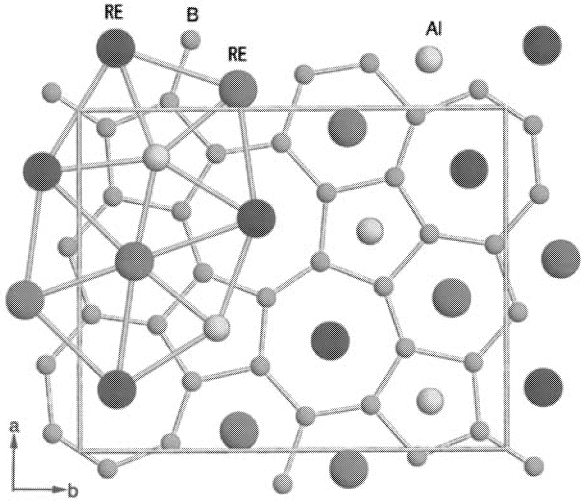

Fig.2 The crystal structure of Lu_2AlB_6.

reside in the interstitial sites of trigonal prisms, formed by the RE (RE = Tm, Yb, Lu) and Al atoms. Tm, Yb and Lu were selected as rare earth elements from the heavy region of the lanthanide series because of the narrow range of their atomic size. In this paper, we report the optimum experimental conditions for growing relatively large crystals of $REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6, starting from RE_2O_3 (RE = Tm, Yb, Lu), crystalline boron powder and an Al self-flux under an argon atmosphere. The size, morphology, chemical analyses, and crystallographic data of the grown crystals were determined. Furthermore, we investigate Vickers microhardness at room temperature and magnetic susceptibility of these compounds at low temperatures.

2. Experimental details

$REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6 crystals were prepared from RE_2O_3 powder (RE = Tm, Yb, Lu) (99.9 % purity) (particle size 0.5 μm), crystalline boron powder (99 % purity) (particle size 5-250 μm) and aluminum chips (99.99 % purity). RE_2O_3 and B powders were weighed in with atomic ratios n = B/RE = 1.0-8.0 according to the reaction

$$RE_2O_3 + (2n+3)B \rightarrow 2REB_n + 3BO. \text{ -------- (1)}$$

Al metal was added to each mixture at a mass ratio of 1:15. From the above preliminary experimental results, the optimum growth conditions of $REAlB_4$ and Lu_2AlB_6 are shown in Table 1. The mixture of starting materials was placed in a high density alumina (99.9 % purity) crucible and heated under an Ar atmosphere. The temperature of the furnace was raised at a rate of 300 K h^{-1} up to 1773 K and held for 10 h at that temperature, and then cooled at a rate of 50 K h^{-1} to 1273 K. Subsequently the furnace was rapidly cooled down to room temperature. The crystals grown in this way were separated from the solidified melts by dissolving the excess Al in hydrochloric acid solution of about 6 mol dm^{-3}.

Table 1 Optimum conditions for growth of $REAlB_4$ and Lu_2AlB_6 crystals from RE-Al-B (RE = Tm, Yb, Lu) melts.

Compounds	Atomic ratio B/RE = n
$TmAlB_4$	2.0
$YbAlB_4$	1.0 or 2.0
$LuAlB_4$	5.5
Lu_2AlB_6	3.0

$REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6 crystals were selected under a stereomicroscope for chemical analyses, measurement of Vickers microhardness, and magnetic susceptibility.

Phase analysis and determination of unit-cell parameters were carried out using a powder X-ray diffractometer (XRD) (Rigaku, RU-200) with monochromatic Cu$K\alpha$ radiation. The morphological properties and impurities of the crystals were investigated by a scanning electron microscope (SEM) (JEOL, T-20) and an energy dispersive X-ray detector (EDX) (Horiba, EMAX-2770). The chemical composition of the crystals grown was determined by means of the inductively coupled plasma (ICP) method (Shimadzu, ICP-50). The density of the crystals was measured using a pycnometer with distilled water at room temperature.

The hardness of the as-grown $REAlB_4$ and Lu_2AlB_6 crystals was measured using a Vickers diamond indenter at room temperature. A load of 0.98 N was applied for 15 s at about 7 positions on relatively large {001} and {100} planes of each crystal, and the obtained values were averaged. Magnetic susceptibility of the as-grown crystals was measured by using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2 K to 300 K under the external magnetic field of 1 kOe [10, 11], with a palladium sample used as a standard.

3. Results and Discussion

3.1 Syntheses of $REAlB_4$ and Lu_2AlB_6 crystals

The B/RE atomic ratio in the starting materials was varied from 1.0 to 8.0. The optimum growth conditions of $REAlB_4$ and Lu_2AlB_6 crystals are shown in Table 1. The variation of the B/RE atomic ratio in the starting materials gave different compounds, and with increased boron concentration, more boron-rich aluminum borides (α-AlB_{12} and β-AlB_{12}) [12, 13] were obtained. However, $REAlB_4$ and Lu_2AlB_6 crystals were obtained as a phase mixture together with REB_4 (RE = Tm or Yb or Lu) or YbB_6 crystals (Fig.3, Fig.4, Fig.5). $REAlB_4$ and Lu_2AlB_6 crystals were generally obtained in the form of a prismatic shape extending in the c direction and with well developed {001} or {100} faces. The crystals have maximum sizes of approximately 0.2 × 3.2 × 3.5 mm for $REAlB_4$ and approximately 0.2 × 0.3 × 3.5 mm for Lu_2AlB_6.

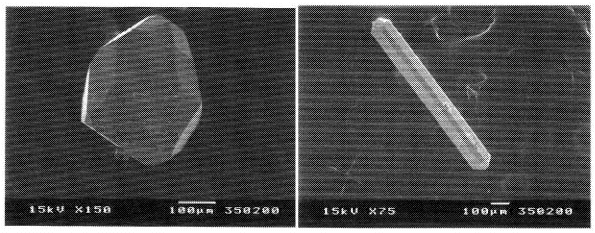

Fig.3 SEM photographs of TmB_4 and $TmAlB_4$ crystals.

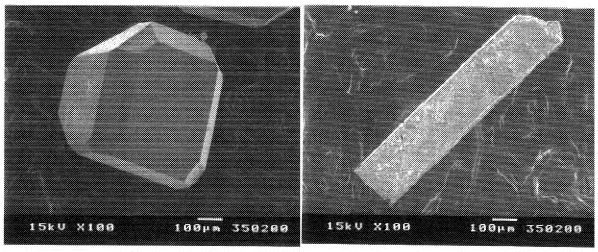

Fig.4 SEM photographs of YbB_6 and $YbAlB_4$ crystals.

The basic crystal data and chemical compositions of $REAlB_4$ and RE_2AlB_6 crystals are listed in Table 2. The well characterized ternary metal boride $TmAlB_4$ and Lu_2AlB_6 have so far not been reported. The diffraction data for $TmAlB_4$ are very similar to those reported for $YbAlB_4$ (a = 0.5927 (2), b = 1.147 (1), and c = 0.3492 (1) nm and $LuAlB_4$ (a = 0.5906 (2), b = 1.144 (1), and c = 0.3480 (1) nm) [2]. The X-ray diffraction data for Lu_2AlB_6 are very similar to those reported for Yb_2AlB_6 (a = 0.9127 (5), b = 1.146 (1), and c = 0.3584 (4) nm) [14].

3.2 Hardness

The results of Vickers microhardness for as-grown $REAlB_4$ and RE_2AlB_6 crystals are listed in Table 3. The microhardness values on the {001} planes of $REAlB_4$ crystals were in the range of 14 to 15 (±1) GPa within the measurement error. The hardness value on the {100} planes of Lu_2AlB_6 crystal is higher than that for $REAlB_4$ and the value of 13 (±1) GPa for Sc_2AlB_6 in the literature [15]. The

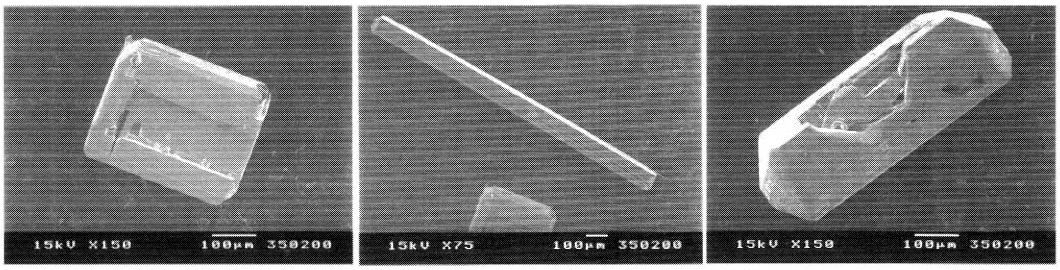

Fig.5 SEM photographs of LuB_4, $LuAlB_4$ and Lu_2AlB_6 crystals.

Table 2 Crystal data and chemical analyses of $REAlB_4$ (RE =Tm, Yb, Lu) and Lu_2AlB_6 crystals.

Formula unit	$TmAlB_4$	$YbAlB_4$	$LuAlB_4$	Lu_2AlB_6
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a (nm)	0.5918(1)	0.5919(1)	0.5898(1)	0.8987(1)
b (nm)	1.1472(1)	1.1465(2)	1.1420(1)	1.1334(1)
c (nm)	0.3477(1)	0.3492(1)	0.3485(1)	0.3633(1)
V (nm^3)	0.2361(1)	0.2369(1)	0.2347(1)	0.3701(1)
Space group	*Pbam*	*Pbam*	*Pbam*	*Pbam*
d_m ($g{\cdot}cm^{-3}$)	6.69(4)	6.78(5)	6.90(4)	7.88(6)
d_x ($g{\cdot}cm^{-3}$)	6.729(2)	6.821(3)	6.939(6)	7.930(5)
Z	4	4	4	4
RE (mass%)	70.9	70.8	71.1	79.2
Al (mass%)	10.2	10.6	17.1	14.5
B (mass%)	17.0	17.6	10.0	5.7
Total (mass%)	98.1	99.0	98.2	99.4
Chemical composition	$TmAl_{0.9}B_{3.8}$	$YbA_{1.0}B_{4.0}$	$LuAl_{0.9}B_{3.9}$	$Lu_2Al_{0.9}B_{5.9}$

Table 3 Vickers microhardness of $REAlB_4$ and Lu_2AlB_6 crystals.

Compound	Load (N)	Vickers microhardness (GPa)
$TmAlB_4$	0.98	15 (± 1)
$YbAlB_4$	0.98	14 (± 1)
$LuAlB_4$	0.98	14 (± 1)
Lu_2AlB_6	0.98	19 (± 1)

Load time: 15 s

linkage of boron atoms in the structures of $YCrB_4$ and Y_2ReB_6-types [14] differs according to the chemical composition. The structure of $YCrB_4$ has boron networks built up by five- and seven-membered rings, and for Y_2ReB_6 has boron networks consisting of five-, six-, and seven-membered rings. Considering the significant difference in structure, especially from Lu_2AlB_6, the difference in the hardness of the aluminum-lutetium boride compounds is noteworthy.

3.3 Magnetic properties

Recently, magnetic behavior has been reported in boron-rich compounds such as REB_{50} [16] and $REB_{22}C_2N$ [17]. We thus investigated the magnetic properties of the new boron-rich system $REAlB_4$ since its properties are completely unknown to date. The magnetic susceptibility of $YbAlB_4$ is shown in Fig.6. As temperature is lowered, the susceptibility increases paramagnetically, but with no large anomalies. A magnetic transition is observed down to 2 K. A small hump below 20 K indicates the presence of small amount of some kind of ferromagnetic impurity phase in the $YbAlB_4$ samples. The nature of this phase is not certainly clear.

The magnetic susceptibility of $TmAlB_4$ is shown in Fig.7. In the same way as $YbAlB_4$, the susceptibility increases paramagnetically as temperature is lowered, but a larger drop in susceptibility is observed at low temperatures, indicating that an anti-ferromagnetic transition has occurred. The transition temperature is determined to be T_N = 5.5 K. This is first magnetic transition observed in this series of samples, and the transition temperature range appears to be similar to that which has been observed for other boron-rich

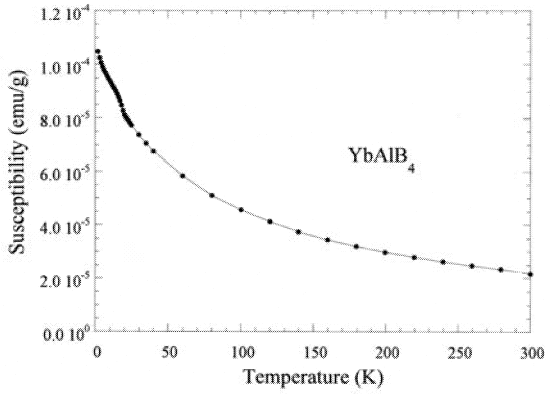

Fig.6 Temperature dependence of the magnetic susceptibility of $YbAlB_4$. (H = 1 kOe)

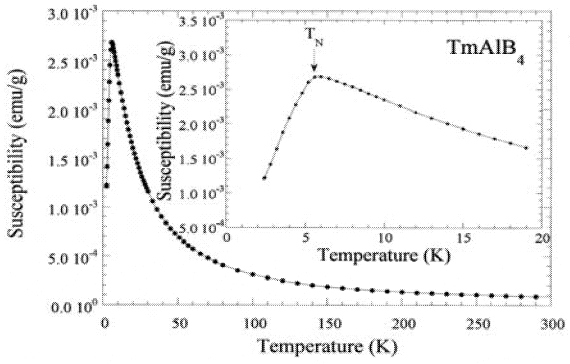

Fig.7 Temperature dependence of the magnetic susceptibility of $TmAlB_4$. (H = 1 kOe)

borides [17].

Although $LuAlB_4$ and Lu_2AlB_6 do not contain atoms with a large magnetic spin, it is nevertheless of interest to investigate the magnetic properties of these new boron-rich compounds. The magnetic susceptibilities of $LuAlB_4$ and Lu_2AlB_6 are shown in Fig.8. The magnetic behavior of $LuAlB_4$ shows little temperature dependence and appears to be dominated by the effects of Pauli paramagnetic susceptibility in metals. The magnetic susceptibility takes a value of 2.2×10^{-6} emu g^{-1} at 300 K. The increase in magnetic susceptibility at low temperatures is indicative of a minor contribution which we attribute to impurities. The impurity component of $LuAlB_4$ appears to be larger than that of Lu_2AlB_6. Finally, we conducted superconductivity measurements on $REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6 crystals down to a temperature of 2 K [18], but superconductivity was not observed.

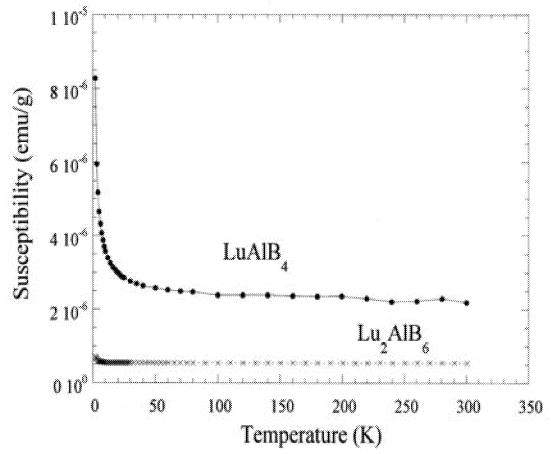

Fig.8 Temperature dependence of the magnetic susceptibility of Lu_2AlB_6 and $LuAlB_4$. (H = 1 kOe)

4. Conclusions

$TmAlB_4$, $YbAlB_4$, $LuAlB_4$ and Lu_2AlB_6 crystals were grown using RE_2O_3 (RE = Tm, Yb, Lu) and crystalline boron in a self-component aluminum melt under an Ar gas at 1773 K for 10 h. The dimensions, morphology and unit-cell parameters of the crystals were examined. The as-grown $REAlB_4$ and Lu_2AlB_6 crystals were investigated for Vickers microhardness at room temperature and magnetic susceptibility from 2 to 300 K. The authors can draw the following conclusion from this study.

(1) $REAlB_4$ and Lu_2AlB_6 crystals were obtained as a phase mixture together with REB_4 (RE = Tm or Yb or Lu) or YbB_6 crystals.

(2) $REAlB_4$ and Lu_2AlB_6 crystals were generally obtained in the form of a prismatic shape extending in the c direction and with well developed {001} or {100} faces The crystals have the maximum sizes of approximately $0.2 \times 3.2 \times 3.5$ mm for $REAlB_4$ and approximately $0.2 \times 0.3 \times 3.5$ mm for Lu_2AlB_6.

(3) The Vickers microhardness values for $REAlB_4$ and Lu_2AlB_6 in several directions on {001} and {100} planes were 14 to 15 (±1) GPa and 19 (±1) GPa, respectively.

(4) The magnetic susceptibility of $REAlB_4$ (RE = Yb, Lu) and Lu_2AlB_6 increases paramagnetically as temperature is lowered. An anti-ferromagnetic transition with a Neel transition temperature of T_N = 5.5 K was found in $TmAlB_4$ crystals.

(5) Superconductivity was not observed in $REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6 compounds down to a temperature of 2 K.

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