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Properties of $REAlB_4$ and Lu_2AlB_6 crystals grown from RE–Al–B (RE = Tm, Yb, Lu) melts

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Abstract

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) and Lu_2AlB_6 crystals were generally obtained in the form of prismatic shape extending in the *c* direction and with well-developed {0 0 1} or {1 0 0} planes. $REAlB_4$ and Lu_2AlB_4 crystals have the maximum size of approximately 3.5 mm. The as-grown crystals were measured for the Vickers microhardness at room temperature and magnetic susceptibility at low temperatures (2–300 K). The values of the Vickers microhardness for $REAlB_4$ and Lu_2AlB_6 in several directions on {0 0 1} and {1 0 0} planes were in the range of 14.0 ± 0.6 to 14.5 ± 1.4 and 18.9 ± 0.7 GPa, respectively. The magnetic susceptibility of $REAlB_4$ (RE = Yb, Lu) and Lu_2AlB_6 increases paramagnetically as temperature is lowered. Superconductivity was not observed in any of the samples down to a temperature of 2 K. An antiferromagnetic transition was found in $TmAlB_4$ with Neel transition temperature of $T_N = 5.5$ K.

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Keywords: $REAlB_4$ (RE = Tm, Yb, Lu); Lu_2AlB_6; Single crystals; Al-self flux; 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*) [1–5]. RE_2AlB_6 and $REAlB_4$ crystals are of great interest because of their remarkable physical and chemical properties, which in many cases are of potential interest for applications to thermoelectric and photodetector materials [6]. However, there is very little information about the physical and chemical properties of RE_2AlB_6 and $REAlB_4$ crystals. $REAlB_4$ has the same structure as that postulated for $YCrB_4$. The linkage of boron atoms in the structures of $YCrB_4$- and 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, 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 reside in the interstitial sites of trigonal prisms, formed by the RE (RE = Tm, Yb, Lu) and Al atoms. Using high-temperature syntheses Al-self components, crystal morphology, chemical analyses, and crystallographic data of the

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Table 1
Conditions for growth of $REAlB_4$ and Lu_2AlB_6 crystals from RE–Al–B (RE = Tm, Yb, Lu) melts

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

as-grown crystals of $REAlB_4$ (RE = Tm, Yb, Lu) and Lu_2AlB_6 were reported previously [3–5]. Here we investigate Vickers microhardness at room temperature and magnetic susceptibility of these compounds at low temperatures.

2. Experimental

$REAlB_4$ (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:

$$RE_2O_3 + (2n + 3)B \rightarrow 2REB_n + BO. \quad (1)$$

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 slowly cooled down 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 with about $6\,mol\,dm^{-3}$ hydrochloric acid.

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

Phase analysis and determination of unit-cell parameters were carried out using a powder X-ray diffractometer (XRD) (Rigaku, RU-200) with monochromatic Cu Kα 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 compositions of the crystals grown were 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.

Measurements on as-grown $REAlB_4$ and Lu_2AlB_6 crystals were done using a Vickers diamond indenter at room temperature. A load of 0.98 N was applied for 15 s at about seven positions on relatively large {0 0 1} and {1 0 0} planes of each crystal, and the values obtained were averaged. Magnetic susceptibility of as-grown crystals was measured by using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2–300 K.

3. Results and discussion

The atomic ratio B/RE in 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 atomic ratio B/RE of starting materials gave different compounds, and with increased boron concentration, more boron-rich aluminum borides (α-AlB_{12} and β-AlB_{12}) [7,8] 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. $REAlB_4$ and Lu_2AlB_6 crystals were generally obtained in the form of prismatic shape extending in the c direction (Fig. 1) and with well-developed {0 0 1} or {1 0 0} planes. The largest crystals have the maximum sizes of approximately 0.2 mm × 3.2 mm × 3.5 mm for $REAlB_4$ and approximately 0.2 mm × 0.3 mm × 3.5 mm for Lu_2AlB_6, respectively.

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 $TmAlB_4$ is very similar to those reported for $YbAlB_4$ (a = 0.5927(2) nm, b = 1.147(1) nm, c = 0.3492(1) nm and $LuAlB_4$ (a = 0.5906(2) nm, b = 1.144(1) nm 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

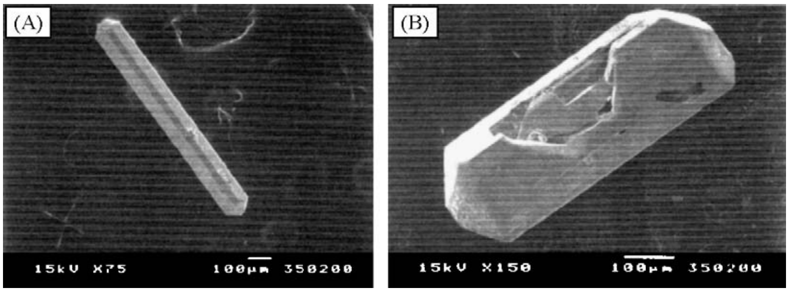

Fig. 1. SEM photographs of $TmAlB_4$ (A) and Lu_2AlB_6 (B) crystals.

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

Formula	$TmAlB_4$	$YbAlB_4$	$LuAlB_4$	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 cm^{-3})	6.69(4)	6.78(5)	6.90(4)	7.88(6)
d_x (g 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	$TmAl_{0.9}B_{3.8}$	$YbAl_{1.0}B_{4.0}$	$LuAl_{0.9}B_{3.9}$	$Lu_2Al_{0.9}B_{5.9}$

(a = 0.9127(5) nm, b = 1.146(1) nm, c = 0.3584(4) nm) [9].

The results of the Vickers microhardness for as-grown $REAlB_4$ and RE_2AlB_6 crystals are listed in Table 3. The microhardness values on the {0 0 1} planes of $REAlB_4$ crystals were in the range of 14.0 ± 0.6 to 14.5 ± 1.4 GPa. The microhardness values of $REAlB_4$ crystals were found to be closely similar. The hardness value of Lu_2AlB_6 crystal is relatively higher than the values for $REAlB_4$ and 12.7 ± 0.8 GPa for Sc_2AlB_6 in the literature [10]. The linkage of boron atoms in the structures of $YCrB_4$ and Y_2ReB_6-types [9] 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.

Recently interesting magnetic behavior has been found in boron-rich compounds such as REB_{50} [11] and $REB_{22}C_2N$ [12]. It is interesting to investigate the magnetic properties of the new boron-rich system $REAlB_4$ since the properties are completely unknown to date. It is also important to check for the presence of superconductivity. The magnetic susceptibility of $YbAlB_4$ is shown in Fig. 2. As temperature is lowered, the susceptibility increases paramagnetically, but no large anomalies. A magnetic transition is observed down to 2 K. A small hump below 20 K indicates that a small amount of a kind of ferromagnetic impurity phase exists in the $YbAlB_4$ samples. It is not clear exactly what this phase is at present.

Table 3
Vickers microhardness of $REAlB_4$ and Lu_2AlB_6 crystals

Compounds	Load (N)	Vickers microhardness (GPa)
$TmAlB_4$	0.98	14.5 ± 1.4
$YbAlB_4$	0.98	14.2 ± 1.4
$LuAlB_4$	0.98	14.0 ± 0.6
Lu_2AlB_6	0.98	18.9 ± 0.7

Load time: 15 s.

The magnetic susceptibility of $TmAlB_4$ is shown in Fig. 3. Similar to $YbAlB_4$, the susceptibility increases paramagnetically as temperature is lowered, but a large drop in the susceptibility is observed at low temperatures indicating that an antiferromagnetic transition has occurred. The transition temperature is determined to be T_N = 5.5 K. This is the first magnetic transition observed in this series of samples, and the

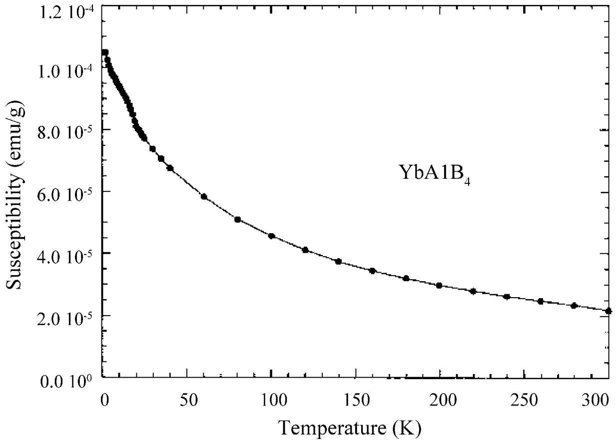

Fig. 2. Temperature dependence of the magnetic susceptibility of $YbAlB_4$.

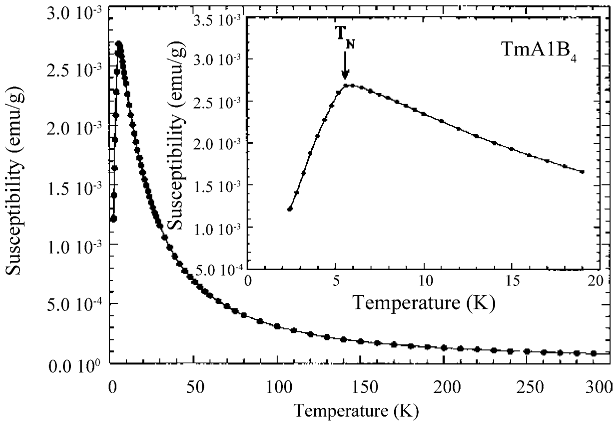

Fig. 3. Temperature dependence of the magnetic susceptibility of $TmAlB_4$.

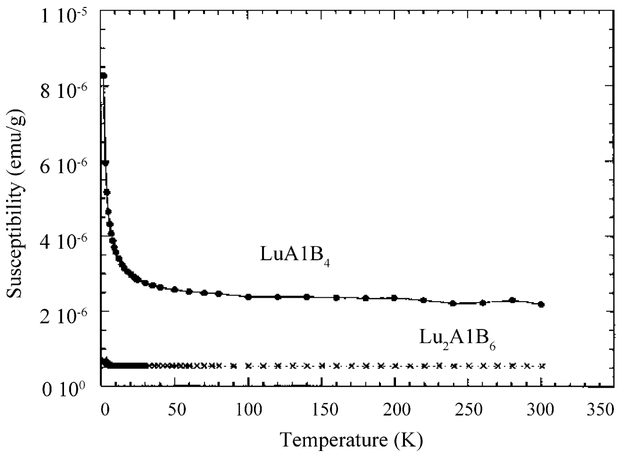

Fig. 4. Temperature dependence of the magnetic susceptibility of Lu_2AlB_6 and $LuAlB_4$.

transition temperature range appears to be similar to what has been observed for other boron-rich borides [12].

Although $LuAlB_4$ and Lu_2AlB_6 do not contain atoms with large magnetic spin, it is interesting to investigate the magnetic properties of these new boron-rich compounds since the properties are completely unknown to date. It is also important to check for the presence of superconductivity. The magnetic susceptibilities of $LuAlB_4$ and Lu_2AlB_6 are shown in Fig. 4. $LuAlB_4$ shows little temperature dependence and appears to be dominated by Pauli paramagnetic susceptibility of metals. The magnetic susceptibility takes a value of 2.2×10^{-6} emu/g at 300 K. The increase 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.

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

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