研究論文　**Original Paper**

Crystal Growth and Characterizations of $AlLiB_{14}$

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Abstract: Single crystals of $AlLiB_{14}$ were grown from a high temperature aluminum solution using $Li_2B_4O_7$ and amorphous boron as raw materials under an argon atmosphere. The $AlLiB_{14}$ crystals obtained had well-developed {010} or {001} faces, and were reddish black with a metallic luster. The maximum dimensions of $AlLiB_{14}$ crystals obtained were about $4.6\times0.3\times0.3$ mm^3. Magnetic susceptibility at low temperature and Vickers micro-hardness of the as-grown crystals were measured, and the oxidation resistance in air at high temperatures was studied. The values of Vickers micro-hardness are in the ranges of 20.2 ± 0.5 GPa to 28.6 ± 0.4 GPa. Oxidation of the $AlLiB_{14}$ starts at 1058 K. The weight gain of the compound after TG determination is 40.8 mass %. A mixture of $Li_2B_2O_4$, $Al_8B_2O_{15}$ and B_2O_3 is identified by XRD as the final oxidation product, and thus the exothermic peak is attributed to oxidation products. The susceptibility of $AlLiB_{14}$ is diamagnetic (-4.4×10^{-7} emu g^{-1}) at 300 K, and the result of magnetic susceptibility measurement at low temperatures of the compound are discussed.

Keywords: $AlLiB_{14}$, single crystal, aluminum flux, Vickers micro-hardness, thermal property, magnetic property

1. Introduction

In the ternary Al–Li–B system, only one type of ternary structure, namely $AlLiB_{14}$ ($AlMgB_{14}$-type, orthorhombic, space group Imam (74)) has been reported so far.[1,2] Boron-rich compounds consisting of B_{12} icosahedra are of great interest because of their remarkable physical and chemical properties, which in many cases are of potential interest for applications to thermoelectrics and photodetectors.[3,4] However, there is very little information about the physical and chemical properties of $AlLiB_{14}$. The anisotropic nature of hardness was measured because it is related to the difference in the number of B_{12} icosahedral units and B-B bonds for linkage of boron atoms in the structure. To determine whether these materials can be used in air at high temperatures, oxidation processes were measured. Interesting magnetic behavior has been observed previously in other B_{12} icosahedral compounds so magnetic characterization of the sample was performed, since nothing of the magnetic properties of this compound is known.

In our previous work, we prepared $AlLiB_{14}$ single crystals from lithium metal chips and crystalline boron powder using an aluminum solution.[2] However, until now there have been no reports on the growth of $AlLiB_{14}$ crystals from anhydrous lithium tetraborate $Li_2B_4O_7$ and amorphous boron powders as the starting materials using a high temperature aluminum flux.

In this paper, we report the experimental conditions for growing relatively large crystals of $AlLiB_{14}$ from $Li_2B_4O_7$ and amorphous boron by slow cooling using an aluminum self-flux under an argon atmosphere. $Li_2B_4O_7$ is selected as the raw material of the lithium element because of its low melting point, its relative chemical stability in air, and its good solubility in an aluminum flux at high temperature. Furthermore, the obtained crystals are easily uncovered by dissolving the Al matrix in dilute hydrochloric acid. The present study of $AlLiB_{14}$ crystal growth is the first to successfully utilize $Li_2B_4O_7$ and boron powders as starting materials in Al self-flux. The size, morphology and crystal-

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lographic data of the crystals were determined. Vickers micro-hardness, oxidation resistance in air up to 1473 K and magnetic susceptibility measurements at low temperature were investigated.

2. Experimental details

The reagents used to prepare the samples were anhydrous lithium tetraborate $Li_2B_4O_7$ (purity 99.8%), amorphous boron (purity 99.9%) and aluminum metal chips (purity 99.99%). $Li_2B_4O_7$ and B were weighted at nominal composition of atomic ratios n = B/Li = 0.2-10 (Table 1) by the reaction shown below:

$$Li_2B_4O_7 + (2n+3)B \longrightarrow 2LiB_n + 7BO. \quad (1)$$

Al metal was added to each mixture at a mass ratio of 1 : 15. The amount of $Li_2B_4O_7$ in the starting materials was fixed at 1.5 g throughout all the experiments. The mixture was placed in a dense alumina crucible and heated in an argon atmosphere. The mixture was heated at a rate of 300 K h^{-1} and held at 1773 K for 5 h. The metal solution was cooled slowly to 1273 K at a rate of 50 K h^{-1} and then furnace cooled to room temperature. The crystals were separated by dissolving excess Al in dilute hydrochloric acid.

Phase analysis and determination of unit cell parameters were carried out by a powder X-ray diffractometer (XRD) (Rigaku, RINT－2500VHF) with monochromatic Cu K_α radiation and a Guinier-Hägg focusing X-ray powder diffraction camera (XDC−1000) with strictly monochromatic Cu $K_{\alpha 1}$ radiation and silicon (purity 99.9999%) as an internal calibration standard. The morphology of as-grown crystals were examined in a four-circle type automatic diffractometer (Rigaku, AFC−6) with graphite monochromatized Mo K_α ($\lambda = 0.0710678$ nm). The morphology, the dimensions and the impurity content of the crystals were examined by a stereomicroscope and a scanning electron microscope (SEM) equipped with an energy-dispersive detector (EDX) (Horiba, EMAX−2770). $AlLiB_{14}$ crystals were selected under a stereomicroscope for the measurement of certain properties.

The Vickers micro-hardness of the crystals was measured at room temperature. A load of 2.94 N was applied for 15 s at about seven points, and the values were averaged.

The oxidation resistance of the sample was studied by differential thermal analysis and thermogravimetric (DTA-TG) measurement in air at the heating rate of 10 K min^{-1}. The oxidation products were analyzed by powder XRD.

The magnetic susceptibility of a pulverized $AlLiB_{14}$ crystal was measured in a field of 1 kG using a commercial superconducting quantum interference device (SQUID) magnetometer in the temperature range of 1.8 K to 300 K.

3. Results and discussion

3.1 Grystal growth of $AlLiB_{14}$

The results of the phase analysis are listed in Table 1. As seen from Table 1, $AlLiB_{14}$, α–AlB_{12}[5] and an unknown phase were formed. Figure 1 shows the powder XRD pattern of $AlLiB_{14}$ crystals. It is likely that the majority of α–Al_2O_3 came from minute fragments of the alumina crucible sticking to the crystals and from the Al_2O_3 mortar used

Table 1 Growth conditions of $AlLiB_{14}$ crystals obtained using $Li_2B_4O_7$ and amorphous boron powders as the starting materials in an Al flux.

Run no.	Composition of the starting material (atomic ratio) Li	B	Phases identified
1	1	0.2	$AlLiB_{14}$, unknown, α–AlB_{12}
2	1	0.5	$AlLiB_{14}$, unknown, α–AlB_{12}
3	1	1.0	$AlLiB_{14}$, unknown, α–AlB_{12}
4	1	2.0	$AlLiB_{14}$, unknown, α–AlB_{12}
5	1	4.0	$AlLiB_{14}$, unknown, α–AlB_{12}
6	1	6.0	$AlLiB_{14}$, unknown, α–AlB_{12}
7	1	8.0	$AlLiB_{14}$, unknown, α–AlB_{12}
8	1	10.0	$AlLiB_{14}$, unknown, α–AlB_{12}

Al metal was added to each mixture at a mass ratio of 1 : 15. The amount of $Li_2B_4O_7$ in the starting materials was fixed at 1.5 g throughout all the experiments.

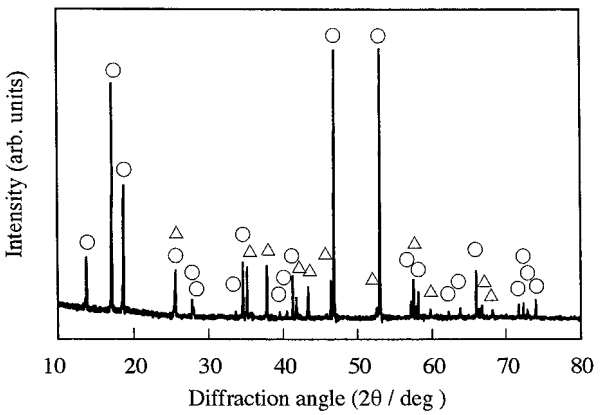

Fig. 1. Powder XRD pattern of $AlLiB_{14}$ crystal. ○: $AlLiB_{14}$, △: α–Al_2O_3

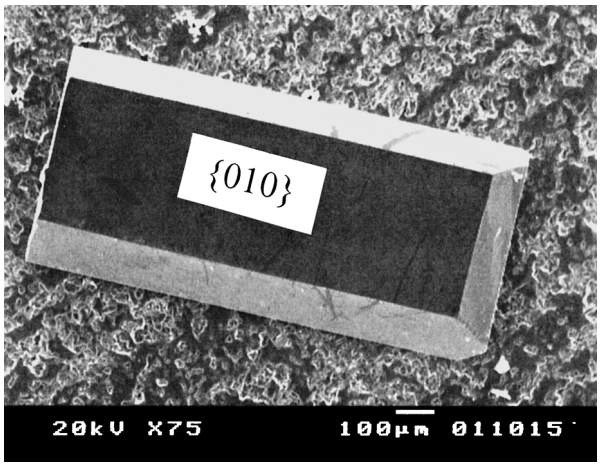

Fig. 2. SEM micrograph of an $AlLiB_{14}$ single crystal (Run no. 3).

Table 2 Unit cell parameters of $AlMgB_{14}$ type crystals.

Formula unit	Space group	Unit cell parameter (nm)			V ($\times 10^{-3}$ nm^3)	Ref.
		a	b	c		
$AlLiB_{14}$	Imam	0.5847(1)	0.8143(1)	1.0354(1)	493.0(1)	This work
$AlLiB_{14}$	Imam	0.58469(9)	0.81429(8)	1.03542(6)	492.97(9)	(2)
$AlMgB_{14}$	Imam	0.5848(1)	0.8112(1)	1.0312(1)	489.2(1)	(2)

Table 3 Vickers micro-hardness of $AlLiB_{14}$ crystals.

Compound	Indentation plane	Hardness (GPa)	Ref.
$AlLiB_{14}$	{001}	28.6 ± 0.4	This work
	{010}	25.5 ± 0.3	This work
	{100}	20.2 ± 0.5	This work
$AlLiB_{14}$	{001}	29.1 ± 0.2	(2)
	{010}	24.5 ± 0.3	(2)

to pulverize the crystals. The $AlLiB_{14}$ crystals obtained had well-developed {010} or {001} faces, and were reddish black (Figure 2). The maximum dimensions of the $AlLiB_{14}$ crystals obtained were about $4.6 \times 0.3 \times 0.3$ mm^3. The crystal structure of this compound is orthorhombic ($AlMgB_{14}$ structure type; space group Imam) with $a =$ 0.5847(1) nm, $b = 0.8143(1)$ nm and $c = 1.0354(1)$ nm, $V =$ $493.0(1) \times 10^{-3}$ nm^3 (Table 2). The unit cell parameters of the compound obtained are in good agreement with data published previously.[2] The impurity content of the $AlLiB_{14}$ crystals was not analyzed chemically. However, no evidence has been obtained of the presence of an oxygen-containing phase within the crystals, as concluded from EDX analysis of as-grown crystals.

3.2 Properties

The values of Vickers micro-hardness of the crystals are listed in Table 3. The values obtained are in the ranges of 20.2 ± 0.5 GPa, 25.5 ± 0.3 GPa and 28.6 ± 0.4 GPa for {100} face, {010} face and {001} face, respectively. The values measured on {010} and {001} faces of the crystals are in comparatively good agreement with the values of these faces for $AlLiB_{14}$ in the literature.[2] However, the value measured on the {100} face of $AlLiB_{14}$ is in the range of 20.2 ± 0.5 GPa, which is noticeably lower than that observed on the {010} and {001} faces. This anisotropic nature of hardness seems to be related to the difference in the number of B_{12} icosahedral units and B-B bonds for linkage of boron atoms in the structures.

The oxidation process of $AlLiB_{14}$ crystals was studied at temperatures below 1473 K by DTA-TG,[6,7] and the results are shown in Figure 3. Oxidation of the sample starts at 1058 K. The weight gain of the compound after TG determination is 40.8 mass%. The DTA curve reveals that one large exothermic peak appears at 1229 K. A mixture of $Li_2B_2O_4$, $Al_8B_2O_{15}$ and B_2O_3 is identified by XRD as the final oxidation product, and thus the exothermic peak is attributed to oxidation products. Data of the oxidation

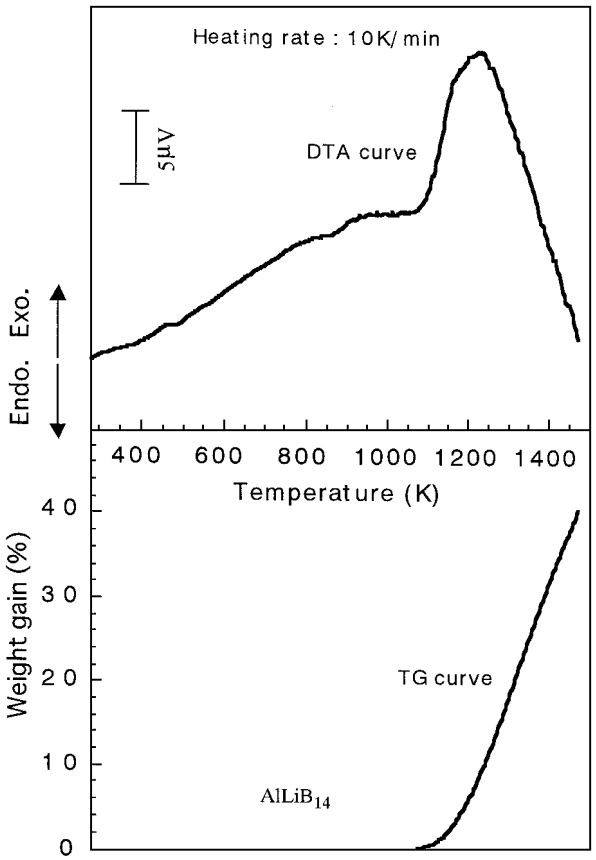

Fig. 3. TG–DTA curves for $AlLiB_{14}$. Samples are heated in air up to 1473 K at 10 K min^{-1}.

resistance of boron-rich compounds consisting of B_{12} icosahedra have not been reported previously.

Recently, interesting magnetic behavior was found in B_{12} icosahedral compounds such as REB_{50} (RE = rare earth)[8] and TbB_{25}.[9] It was indicated that magnetic interaction is mediated by the B_{12} icosahedra.[8] This is a completely new phenomenon in boride compounds and the mechanism is still being studied. Although there are no atoms with large magnetic spin among the $AlLiB_{14}$ compounds, it is important to characterize the magnetic properties of this new B_{12} icosahedral compound, which has a structure similar to TbB_{25},[9] since the properties have been completely unknown to date until now. The temperature dependence of the magnetic susceptibility was measured down to 2 K, and the result is shown in Figure 4. The susceptibility of $AlLiB_{14}$ is diamagnetic (-4.4×10^{-7} emu g^{-1} at 300 K)[10] and shows an increase at low tempera-

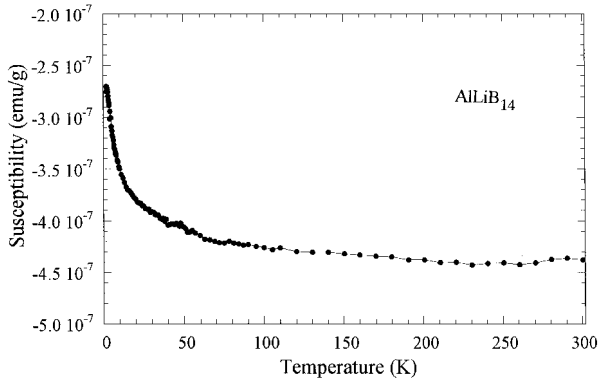

Fig. 4. Temperature dependence of the magnetic susceptibility of $AlLiB_{14}$.

tures indicative of a small paramagnetic contribution, which we attribute to impurities.

4. Conclusion

Single crystals of $AlLiB_{14}$ were grown from a high temperature aluminum solution using $Li_2B_4O_7$ and amorphous boron as raw materials under an argon atmosphere. The mixture of starting materials were heated at rate of 300 K h^{-1} and held at 1773 K for 5 h. The metal solution was cooled slowly to 1273 K at a rate of 50 K h^{-1} and then furnace cooled to room temperature. The size, morphology and crystallographic data of the crystals were determined. Vickers micro-hardness, oxidation resistance in air up to 1473 K and magnetic susceptibility measurements at low temperatures were investigated. The authors can draw the following conclusion from this study.

1) The mixtures of $Li_2B_4O_7$ and B powders were weighted at nominal composition of atomic ratios B/Li = 0.2–10, and $AlLiB_{14}$, α–AlB_{12} and an unknown phase were formed.
2) The $AlLiB_{14}$ crystals had well developed {010} or {001} faces, and were reddish black. The maximum dimensions of the crystals were about $4.6 \times 0.3 \times 0.3$ mm^3.
3) The crystal structure of $AlLiB_{14}$ is orthorhombic ($AlMgB_{14}$ structure type; space group Imam) with $a = 0.5847(1)$ nm, $b = 0.8143(1)$ nm, $c = 1.0354(1)$ nm, and $V = 493.0(1) \times 10^{-3}$ nm^3.
4) The values of Vickers micro-hardness are in the ranges of 20.2 ± 0.5 GPa, 25.5 ± 0.3 GPa and 28.6 ± 0.4 GPa for {100} face, {010} face and {001} face, respectively.
5) The oxidation of $AlLiB_{14}$ starts at 1058 K. The weight gain of the compound after TG determination is 40.8 mass%. A mixture of $Li_2B_2O_4$, $Al_8B_2O_{15}$ and B_2O_3 is identified by XRD as the final oxidation product.
6) The susceptibility of $AlLiB_{14}$ is diamagnetic (-4.4×10^{-7} emu g^{-1}) at 300 K, and shows an increase at low temperatures indicative of a small paramagnetic contribution.

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