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Crystal growth of a new aluminum sodium boride $NaAlB_{14}$ and some properties

Shigeru Okada [a,*], Takao Mori [b], Kunio Kudou [c], Takaho Tanaka [b], Toetsu Shishido [d], Torsten Lundström [e]

[a] Faculty of Engineering, Kokushikan University, 4-28-1 Setagaya, Setagaya-ku, Tokyo 154-8515, Japan
[b] National Institute for Materials Science, 1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan
[c] Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yohohama 221-8686, Japan
[d] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-0812, Japan
[e] The Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

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Abstract

Single crystals of a new ternary boride $NaAlB_{14}$ were obtained from the Na-Al-B system using a high-temperature Al self-flux under an Ar atmosphere. The reagents used to prepare the samples were $Na_2B_4O_7$ powder, crystalline boron powder and Al metal chips. The optimum conditions to obtained relatively large crystals were found to include soaking temperature 1573 K, soaking time 1 h, cooling rate 50 K/h and the atomic ratios (n = B/Na = 1.0–4.0) of starting materials. The $NaAlB_{14}$ crystal prepared had maximum sizes of approximately 7.3 mm × 3.3 mm × 2.8 mm. The crystals were generally obtained in the form of plate-like crystals with well-developed {0 1 0} faces or trapezoidal-shape crystals enclosed by {1 0 0}, {0 1 0}, {0 1 1} and {0 0 1} faces, and were reddish black with a metallic luster. The values of Vickers microhardness are in the ranges of 23.3 ± 1.0 and 28.4 ± 0.6 GPa for {1 0 0} and {0 1 0} faces, respectively. The susceptibility does not show any particular features, but an increase at low temperatures is indicative of a paramagnetic contribution.

Keywords: X-ray methods; Hardness; Magnetic properties; Boride; Refractories

1. Introduction

Boron-rich compounds containing B_{12} icosahedral structural units are of great interest because of their remarkable physical and chemical properties, which in many cases are of potential interest for applications to thermoelectric materials and photodetectors.[1] However, there is very little information about chemical and physical properties of boron-rich borides. Recently we successfully prepared single crystals of a new ternary boride $NaAlB_{14}$ from the high-temperature Al self-flux using an anhydrous sodium tetraborate $Na_2B_4O_7$ and crystalline boron powders as the raw materials. In this paper, we report the detailed experimental conditions for growing crystals of $NaAlB_{14}$ from the high temperature Al self-flux using $Na_2B_4O_7$ and crystalline boron powders as the raw materials. The size, morphology and powder X-ray diffraction data of $NaAlB_{14}$ crystals were determined. Magnetic susceptibility at low temperatures and Vickers microhardness at room temperature of the as-grown crystals were investigated. The present study of $NaAlB_{14}$ crystals is the first study of their physical properties. $Na_2B_4O_7$ is more suitable as a source of sodium element than Na metal that has high vapor pressure,[2] because of relatively high chemical stability in air, low reactivity for an alumina crucible at high temperature, and good solubility in the Al solution at high temperature.

2. Experimental details

The reagents used to prepare the compounds were anhydrous sodium tetraborate $Na_2B_4O_7$ (purity 99%) powder, crystalline boron (purity 99%) powder and aluminum metal

* Corresponding author. Tel.: +81 3 5481 3292; fax: +81 3 5481 3292.
E-mail address: sokada@kokushikan.ac.jp (S. Okada).

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Table 1
Typical growth conditions of $NaAlB_{14}$

Run no.	Composition of the starting material (atomic ratio)		Phases identified
	Na	B	
1	1	1.0	$NaAlB_{14}$
2	1	2.0	$NaAlB_{14}$
3	1	4.0	$NaAlB_{14}$
4	1	6.0	$NaAlB_{14}$, AlB_2
5	1	8.0	$NaAlB_{14}$, α-AlB_{12}, AlB_2
6	1	10.0	α-AlB_{12}, AlB_2, $NaAlB_{14}$
7	1	12.0	α-AlB_{12}, AlB_2, $NaAlB_{14}$
8	1	14.0	α-AlB_{12}, AlB_2, β-AlB_{12}
9	1	16.0	α-AlB_{12}, β-AlB_{12}, AlB_2
10	1	20.0	α-AlB_{12}, β-AlB_{12}, AlB_2

sticks (purity 99.99%). $Na_2B_4O_7$ and B were weighed at nominal composition of atomic ratios n = B/Na = 1.0–20.0 (Table 1). Al metal was added to each mixture at a mass ratio of 1:15. The amount of $Na_2B_4O_7$ 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 Ar gas. The mixture was heated at a rate of 300 K/h and kept at 1573 K for 1 h. The solution was cooled to 1073 K at a rate of 50 K/h and then the furnace was switched off. Dissolving the solidified mixture in a mixed solution of hydrochloric acid and ethanol separated the grown crystals. $NaAlB_{14}$ crystals were selected under a stereomicroscope for the measurements of chemical analyses, X-ray diffraction, microhardness and magnetic susceptibility. The chemical composition of $NaAlB_{14}$ crystals grown in the Al-self flux was determined by the electron probe microanalysis (EPMA)[3] using standards of a single-crystal $NaAlSi_3O_8$ for Na and Al, and a single-crystal $B_{4.5}C$ for B. Standard deviations of the EPMA measurement were ±1% for each element. The morphological properties and impurities of the crystals were investigated by a scanning electron microscope (SEM) and an energy dispersive X-ray detector (EDX).[4] Phase identification and determination of unit-cell parameters were carried out using a standard powder X-ray diffractometer (XRD) with monochromatic Cu Kα radiation. As-grown $NaAlB_{14}$ crystals were measured using a Vickers diamond indenter[5] at room temperature. A load of 1.96 N was applied for 15 s at about eight positions on relatively large {1 0 0} and {0 1 0} faces of each crystal. The magnetic susceptibility of a pulverized $NaAlB_{14}$ crystal was measured by using a superconducting quantum interference device (SQUID) magnetometer[6,7] in the temperature range of 2–300 K.

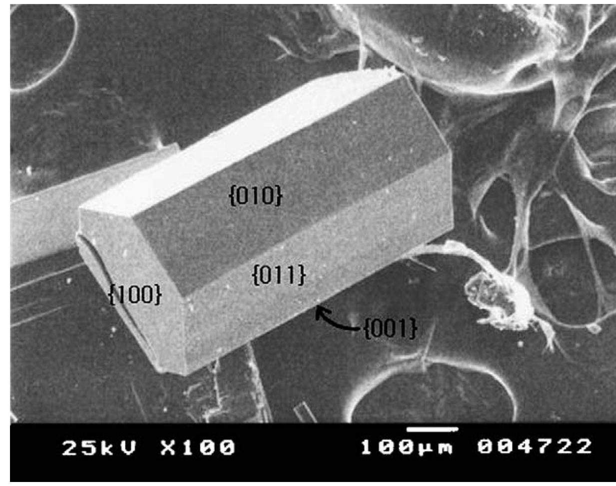

Fig. 1. SEM photograph of $NaAlB_{14}$ crystal (run no. 2).

3. Results and discussion

Experimental conditions for the single crystal growths are shown in Table 1. As seen from Table 1, $NaAlB_{14}$, AlB_2,[1] α-AlB_{12}[8] and β-AlB_{12}[1] crystals were formed. $NaAlB_{14}$ crystals could be grown under the conditions of run no. 1–7 (atomic ratios n = B/Na = 1.0 to 12.0). $NaAlB_{14}$ crystals were obtained as single phase product for atomic ratios n = B/Na = 1.0–4.0. The $NaAlB_{14}$ crystal prepared had maximum sizes of approximately 7.3 mm × 3.3 mm × 2.8 mm. $NaAlB_{14}$ crystals were generally obtained in the form of plate-like crystals with well-developed {0 1 0} faces. Single crystal having the typical crystal form is shown in Fig. 1. They are enclosed by two large {0 1 0} faces, two small {0 0 1} faces, two large {0 1 1} faces and two large {1 0 0} faces. The colour was brick-red with a metallic luster.

Unit-cell parameters for $MgAlB_{14}$-type compounds were collected in Table 2. The powder XRD indexing result indicated that the grown $NaAlB_{14}$ crystals have

Table 2
Unit-cell parameters of $MgAlB_{14}$-type compounds

Compounds	Unit-cell parameters (nm)			V (nm^3)	References
	a	b	c		
$NaBB_{14}$	0.5847	0.8415	1.0298	0.5067	9
$LiAlB_{14}$	0.5847(1)	0.8143(1)	1.0354(1)	0.4930(1)	10
	0.58469(9)	0.81429(8)	1.03542(6)	0.49297(8)	11
$MgAlB_{14}$	0.5848(1)	0.8112(1)	1.0312(1)	0.4892(1)	12
	0.58450(2)	0.81137(7)	1.03298(4)	0.4899(1)	13
$NaAlB_{14}$	0.5844(1)	0.8231(1)	1.0465(1)	0.5034(1)	This work

Table 3
Chemical analysis data of $NaAlB_{14}$ crystal

Compound	Crystal	Chemical analysis (mass%)			In total	Chemical composition
		Na	Al	B		
$NaAlB_{14}$	Plate	11.90	13.19	78.09	103.18	$Na_{1.00}Al_{0.95}B_{14}$

an orthorhombic crystal structure with unit-cell parameters of $a = 0.5844(1)$ nm, $b = 0.8231(1)$ nm, $c = 1.0465(1)$ nm. The unit-cell parameters of $NaAlB_{14}$ are very similar to those reported for $NaBB_{14}$,[9] $LiAlB_{14}$[10,11] and $MgAlB_{14}$[12,13] (Table 2). Chemical analysis for the crystal corresponds to an atomic ratio Na:Al:B = 1:1:14 (Table 3). No evidence has been obtained for the presence of an oxygen containing phase in the crystals, as concluded from EDX and EPMA analyses of as-grown crystals. Powder X-ray diffraction intensities for $NaAlB_{14}$ are presented in Table 4 together with observed and calculated interplanar spacings (d_{obs} and d_{calc}, respectively). The diffraction data for $NaAlB_{14}$ are very similar to those reported for $LiAlB_{14}$[11] and $MgAlB_{14}$[12].

The values of Vickers microhardness of the crystals are listed in Table 5. The values obtained are in the ranges of 23.3 ± 1.0 and 28.4 ± 0.6 GPa for {1 0 0} and {0 1 0} faces, respectively. The values measured on {1 0 0} and {0 1 0} faces of the crystals are in comparatively good agreement with the values of these faces for $LiAlB_{14}$ and $MgAlB_{14}$ in the literature.[10,13] However, the value measured on the {1 0 0} face of $NaAlB_{14}$ is in the range of 23.3 ± 1.0 GPa, which is noticeably lower than that observed on the {0 1 0} face. This anisotropic nature of hardness seems to be related to the difference in the number of B_{12} icosahedral units and boron–boron bonds for linkage of boron atoms in the structures.

Recently, interesting magnetic behavior has been observed in B_{12} icosahedral compounds like $REB_{22}C_2N$ (RE = rare earth)[14] and TbB_{25}.[6] It has been indicated that the magnetic interaction is mediated by the B_{12} icosahedra[14] which is a completely new phenomena in boride compounds. The structure of $NaAlB_{14}$ is similar to TbB_{25} in which an antiferromagnetic-like transition was discovered at 2.1 K.[6] Although there are no atoms with large magnetic spin in $NaAlB_{14}$, it is important to characterize the magnetic properties of such new B_{12} compounds, since the magnetic properties are completely unknown to date. The temperature dependence of the magnetic susceptibility of $NaAlB_{14}$ was measured from 300 to 2 K and is shown in Fig. 2. The susceptibility does not show any particular features, with an increase at low temperatures indicative of a paramagnetic contribution. The origin of such a contribution can usually be thought to be impurities but an interesting point is that the susceptibility is very similar to the previous measured compound of $LiAlB_{14}$,[10] while both compounds have a much smaller paramagnetic part than the $MgAlB_{14}$ compound,[13] as can be seen in the inset of Fig. 2. To make clear whether this is an intrinsic difference between the alkali metal containing com-

Table 4
Powder X-ray diffraction data of $NaAlB_{14}$

h	k	l	d_{calc} (nm)	d_{obs} (nm)	$I_{obs.}$
1	0	1	0.64696	0.64771	46
2	0	0	0.52325	0.52358	8
0	1	1	0.47651	0.47716	26
0	0	2	0.41155	0.41183	6
2	1	1	0.35231	0.35256	36
2	0	2	0.32348	0.32361	25
1	2	1	0.26630	0.26650	39
4	0	0	0.26163	0.26192	2
2	2	0	0.25512	0.25531	30
0	1	3	0.24836	0.24873	3
3	1	2	0.24218	0.24225	25
0	2	2	0.23826	0.23818	5
4	1	1	0.22933	0.22940	8
2	1	3	0.22437	0.22446	57
4	0	2	0.22079	0.22088	23
2	2	2	0.21683	0.21692	44
3	2	1	0.21614	0.21622	100
5	0	1	0.20284	0.20282	7
4	2	0	0.19491	0.19490	5
1	1	4	0.19084	0.19095	12
0	3	1	0.18956	0.18975	3
4	1	3	0.18012	0.18024	2
5	1	2	0.17772	0.17769	13
4	2	2	0.17616	0.17628	8
6	0	0	0.17442	0.17447	35
1	3	2	0.17369	0.17373	17
0	2	4	0.16824	0.16834	17
5	2	1	0.16663	0.16665	13
1	0	5	0.16262	0.16269	8
6	0	2	0.16059	0.16061	6
2	2	4	0.16017	0.16025	18
0	3	3	0.15884	0.15903	12
4	3	1	0.15350	0.15364	2
6	2	0	0.14976	0.14978	19
7	0	1	0.14709	0.14709	6
0	4	0	0.14610	0.14613	4
6	1	3	0.14273	0.14270	4
1	2	5	0.14210	0.14216	5
4	2	4	0.14151	0.14154	5
6	2	2	0.14074	0.14079	6
1	3	4	0.14019	0.14032	7
0	4	2	0.13768	0.13769	3
0	0	6	0.13718	0.13732	4
7	1	2	0.13662	0.13669	8
4	3	3	0.13577	0.13582	2
5	3	2	0.13474	0.13483	9
2	4	2	0.13315	0.13321	5
2	0	6	0.13270	0.13271	10
7	2	1	0.13139	0.13143	7
7	0	3	0.13128	0.13133	7
3	3	4	0.13110	0.13109	3
5	0	5	0.12939	0.12941	9
1	4	3	0.12799	0.12804	2
8	1	1	0.12615	0.12619	5
3	1	6	0.12472	0.12473	4
4	4	2	0.12184	0.12187	4
3	4	3	0.12096	0.12101	14
7	3	0	0.11860	0.11866	3
8	1	3	0.11574	0.11579	3
8	2	2	0.11467	0.11472	2
2	1	7	0.11258	0.11261	2
4	2	6	0.11218	0.11209	5
7	0	5	0.11067	0.11069	3

Table 5
Vickers microhardness of $NaAlB_{14}$ crystals

Compound	Indentation plane	Hardness value (GPa)	Reference
$NaAlB_{14}$	{1 0 0}	23.3 ± 1.0	This work
	{0 1 0}	28.4 ± 0.6	This work
$LiAlB_{14}$	{1 0 0}	20.2 ± 0.5	10
	{0 1 0}	25.5 ± 0.3	10
	{0 0 1}	28.6 ± 0.4	10
$MgAlB_{14}$	{1 0 0}	23.9 ± 0.6	13
	{0 1 0}	25.5 ± 0.5	13
	{0 0 1}	27.6 ± 0.6	13

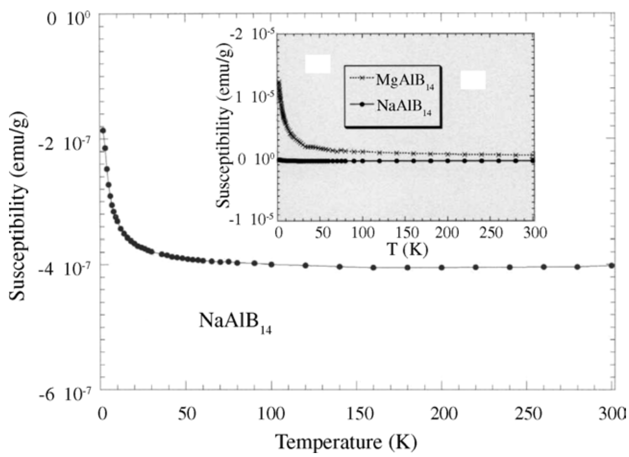

Fig. 2. Magnetic susceptibility of $NaAlB_{14}$. For comparison, the susceptibility of $MgAlB_{14}$ is plotted together in the inset.

pounds and alkaline-earth metal containing compounds, we are trying to make detailed analysis of the impurity contents of this series of compounds.

4. Conclusions

The single crystals of $NaAlB_{14}$ were grown using anhydrous sodium tetraborate and crystalline boron as starting materials in a self-component aluminum solution under an argon atmosphere. The $NaAlB_{14}$ crystals were generally obtained in the form of plate-like crystals with well-developed {0 1 0} faces or trapezoidal-shape crystals enclosed by two large {0 1 0} faces, two small {0 0 1} faces, two large {0 1 1} faces and two large {1 0 0} faces. The colour was brick-red with a metallic luster. The crystal structure of this compound is orthorhombic ($MgAlB_{14}$ structure type; the space group *Imma* (no. 74)) with $a = 0.5844(1)$ nm, $b = 0.8231(1)$ nm, $c = 1.0465(1)$ nm, $V = 0.5034(1)\,nm^3$. The as-grown $NaAlB_{14}$ crystals were used for measurements of Vickers microhardness at room temperature and magnetic susceptibility at low temperatures. The values of Vickers microhardness are in the ranges of 23.3 ± 1.0 and 28.4 ± 0.6 GPa for {1 0 0} and {0 1 0} faces, respectively. The susceptibility does not show any particular features, but an increase at low temperatures is indicative of a paramagnetic contribution. The present study of $NaAlB_{14}$ crystals is the first physical properties study.

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