

Crystal growth of higher borides from melts in the Al-ME-B (ME = Be, Mg, Cu) or Cu-B systems and its properties

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Abstract: $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$), $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ and CuB_{23} crystals were grown from high-temperature melts of the systems Al-M-B (M = Be, Mg, Cu) and Cu-B in an argon atmosphere. The maximum dimensions of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were obtained in the ranges of approximately 2.5 to 5.2 mm. CuB_{23} crystals prepared had maximum dimensions of approximately 30 μm . The $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ and $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ crystals were obtained as plate-like crystals having well-developed {101} and {001} faces, and $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were obtained in the form of needle or rhombohedral plate as bounded by {001} faces and grew as prismatic shape extending in the c direction. The values of Vickers microhardness on relatively large {101}, {100}, {001} and {001} faces of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals are in the ranges of 25.4 (0.5) to 27.8 (1.7) GPa. The TG curves show that the oxidation of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{2.8}\text{Cu}_{2.9}\text{B}_{105}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$, $\text{Al}_{1.3}\text{Cu}_{1.0}\text{B}_{105}$, $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ and CuB_{23} crystals began to proceed at 1080, 1121, 746, 923, 984, 984 and 722 K, respectively. Anomalous magnetic behavior was not observed for any of the compounds, and the good agreement of the temperature independent susceptibility for the $\text{Al}_x\text{Cu}_y\text{B}_{105}$ compounds with different metal stoichiometries indicate the non-metallic nature of this phase. None of the compounds measured in this work are indicated to be superconducting down to 1.8 K.

Keywords: Higher borides, Melts growth, Vickers microhardness, Oxidation resistance, Magnetic susceptibility

1. Introduction

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 thermoelectric, photodetectors and neutron shelters [1]. In our previous work [2, 3] we successfully prepared single crystals of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ (tetragonal), $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ (orthorhombic), $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) (rhombohedral), $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ (tetragonal) and CuB_{23} (rhombohedral) from high-temperature melts in the Al-M-B (M = Be, Mg, Cu) or Cu-B systems using metals and boron powder as starting materials

by slowly cooling under an argon atmosphere. Those crystals obtained are report for crystal growth and structure refinement [2–4]. However, so far physical and chemical properties of these compounds have not been sufficiently reported. In the present paper, the size and morphology of the crystals determined, and oxidation resistance heated in air, Vickers microhardness at room temperature and magnetic susceptibility at low temperatures of the as-grown crystals were investigated.

2. Experimental details

The reagents used to prepare the compounds and their purities were as follows : Al, 99.99%; Cu, 99.999%; Mg,

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99.999%; Be, 99.5%; B, 99.5%. The mixture of starting materials was placed in the dense Al_2O_3 (99.8%) or hBN (99.9%) crucibles. Each of the starting mixtures with the required composition was placed in an Al_2O_3 crucible. For the Al–Be–B and Cu–B system solutions, BN crucibles were used. The crucible was inserted in a vertical electric furnace with a SiC heater, and heated in an Ar gas. The mixture was heated at a rate of 300 K/h and kept at soaking temperature 1673 K or 1773 K for soaking time 1 h or 3 h. The solution was cooled to 1073 K at a rate of 50 K/h and then the furnace was switched off. The crystals grown in the solidified mixture were separated by dissolving the excess metal solvent Al or Cu with dilute hydrochloric acid (6M–HCl) or nitric acid (6M–HNO₃). $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were selected under a stereomicroscope for chemical analyses and measurements of X-ray diffraction, Vickers microhardness, oxidation resistance and magnetic susceptibility. However, CuB_{23} crystals prepared had maximum dimensions of approximately 30 μm , and not always sufficiently large for some property measurements.

Phases analysis and determination of unit-cell parameters were carried out using a powder X-ray diffractometer (XRD) (Rigaku, RU-200) with monochromatic $\text{CuK}\alpha$ 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 compositions of the crystals grown were determined by means of the inductively coupled plasma method (Shimadzu, ICP-50).

Measurements on as-grown $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were done using a Vickers diamond indenter at room temperature. A load of 1.96 N was applied for 15 s at about eight positions on relatively large {101}, {100}, {001} and {001} faces of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals, and the values obtained were averaged. Pulverized samples of approximately 25 mg were heated between

room temperature and 1473 K in air at a rate of 10 K/min by differential thermal analysis and thermogravimetric (TG/DTA) analyses [7]. The oxidation products were analyzed by a powder XRD. The magnetic susceptibility of the powder samples was measured in a field of 1 kG using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 1.8 to 300 K [8].

3. Results and discussion

The synthesized crystals phases syntheses in the present work are $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$), $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ and CuB_{23} crystals are obtained from melts in the systems Al–M–B (M = Be, Mg, Cu) and Cu–B. Typical experimental conditions and maximum size for growth of the crystals are shown in Table 1. The unit-cell parameters and chemical analyses are presented together with published references in Table 2 and 3. The unit-cell parameters of these compounds are in relatively good agreement with data published previously [2–5]. The chemical compositions obtained by the chemical analysis are approximately equivalent to those obtained at structure analyses [2–4]. Although the impurity content of each crystal was analyzed chemically, EDX established the occurrence of traces of silicon, calcium and iron, combination of oxygen or nitrogen atoms into the obtained crystals, which might come from the Al_2O_3 or BN crucibles, was found to be negligible. The single crystals of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ are shown in Fig. 1. The $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ and $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ crystals were obtained as plate-like crystals having well-developed {101} and {001} faces, and $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were obtained in the form of needle or rhombohedral plate as bounded by {001} faces and grew as prismatic shape extending in the c direction.

The values of Vickers microhardness of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{2.8}\text{Cu}_{2.9}\text{B}_{105}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$, $\text{Al}_{3.3}\text{Cu}_{1.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystal are shown in Table 4. The values obtained are in the ranges of 25.4 (0.5) to 27.8 (1.7) GPa. The microhardness values of each crystals were found to be closely similar. The values of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ crystals meas-

Table 1 Typical growth conditions of higher borides obtained from melts in the systems Al–M–B (M = Be, Mg, Cu) and Cu–B

Compound	Composition of the starting mixture in atomic ratio Al : M (Be, Mg, Cu) : B	Soaking temperature (K) and time (h)	Phases identified	Maximum size (mm)
Al–Be–B*	67 : 1 : 8	1673, 1	$\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$	5.2
Al–Mg–B	40 : 1 : 8	1773, 3	$\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$	4.5
Al–Cu–B**	0 : 20 : 4	1773, 3	$\text{Al}_{2.8}\text{Cu}_{2.9}\text{B}_{105}$	3.5
Al–Cu–B	1 : 20 : 4	1773, 3	$\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$	3.5
Al–Cu–B	4 : 20 : 4	1773, 3	$\text{Al}_{3.3}\text{Cu}_{1.0}\text{B}_{105}$	4.5
Al–Cu–B	0.5 : 5 : 1	1773, 3	$\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$	2.5
Cu–B*	0 : 35 : 1	1773, 3	CuB_{23}	0.03

* hBN crucible was used.

** Al atoms from the Al_2O_3 crucible participated in the growth of the crystal.

Table 2 Crystal data of higher borides

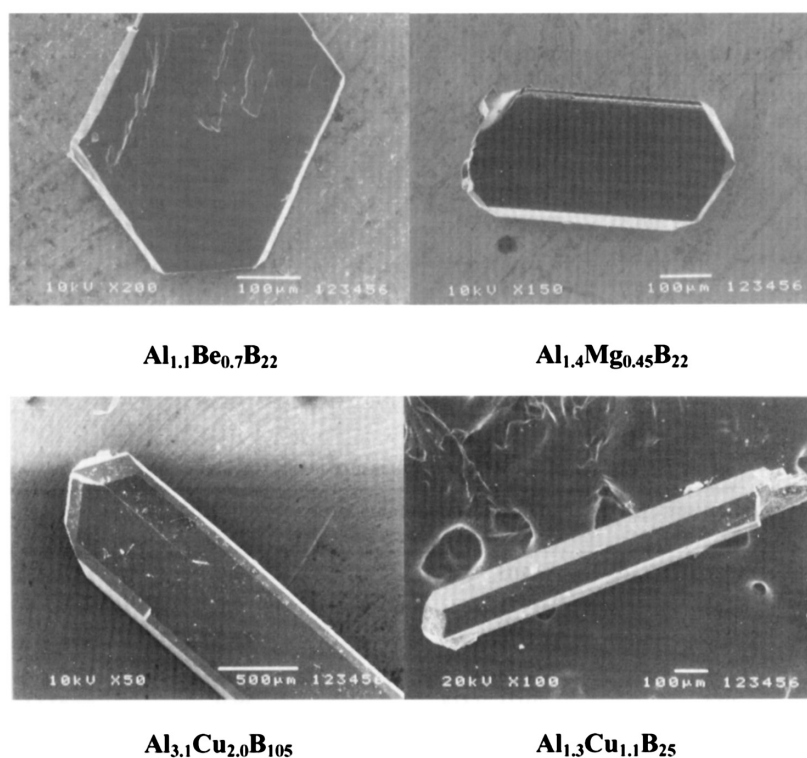
Compound	Crystal system	Unit-cell parameter			Reference
		<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	
Al _{1.1} Be _{0.7} B ₂₂	tetragonal	1.017(1)	—	1.425(1)	This work
Al _{1.2} Be _{0.5} B ₂₂		1.0174(1)	—	1.4235(6)	[2]
Al _{1.4} Mg _{0.45} B ₂₂	orthorhombic	1.663(1)	1.755(1)	1.018(1)	This work
AlMgB ₂₂		1.6633(3)	1.7547(4)	1.0187(2)	[3]
Al _{2.8} Cu _{2.9} B ₁₀₅ *	rhombohedral	1.100(1)	—	2.396(1)	This work
Al _{3.1} Cu _{2.0} B ₁₀₅ *	rhombohedral	1.099(1)	—	2.396(1)	This work
Al _{3.3} Cu _{1.0} B ₁₀₅ *	rhombohedral	1.099(1)	—	2.395(2)	This work
Al _{3.8} Cu _{0.8} B ₁₀₅ *		1.0983(1)	—	2.3928(2)	[3]
Al _{3.7} Cu _{0.8} B ₁₀₅ *		1.0980(1)	—	2.3930(2)	[4]
Al _{1.3} Cu _{1.1} B ₂₅	tetragonal	0.902(3)	—	0.508(2)	This work
Al _{1.5} Cu _{0.7} B ₂₅		0.902(3)	—	0.508(2)	[3]
CuB ₂₃ *	rhombohedral	1.096(1)	—	2.393(1)	This work
CuB ₂₃ *		1.0965(1)	—	2.3925(2)	[5]

* For the rhombohedral unit-cell, hexagonal unit-cell parameters are given.

Table 3 Chemical analyses data of higher borides

Compound	Chemical analysis (mass%)						Chemical composition
	Al	Be	Mg	Fe	Cu	B	
Al _{1.1} Be _{0.7} B ₂₂	10.0	2.7	—	0.08	0.01	Balance	Al _{1.0} Be _{0.8} B ₂₂ *
Al _{1.4} Mg _{0.45} B ₂₂	12.1	—	3.5	—	—	76.4	Al _{1.4} Mg _{0.45} B ₂₂
Al _{2.8} Cu _{2.9} B ₁₀₅	5.4	—	—	0.03	13.0	81.1	Al _{2.8} Cu _{2.9} B ₁₀₅
Al _{3.1} Cu _{2.0} B ₁₀₅	6.1	—	—	0.02	9.2	84.4	Al _{3.1} Cu _{2.0} B ₁₀₅
Al _{3.3} Cu _{1.0} B ₁₀₅	6.8	—	—	0.03	5.1	87.7	Al _{3.3} Cu _{1.0} B ₁₀₅
Al _{1.3} Cu _{1.1} B ₂₅	9.0	—	—	—	17.9	69.1	Al _{1.3} Cu _{1.1} B ₂₅
CuB ₂₃	0.02	—	—	0.02	20.5	79.1	CuB _{22.7}

* Reference [2]

**Fig. 1** SEM photographs of Al_{1.1}Be_{0.7}B₂₂, Al_{1.4}Mg_{0.45}B₂₂, Al_{3.1}Cu_{2.0}B₁₀₅ and Al_{1.3}Cu_{1.1}B₂₅ crystals.

ured are in comparatively good agreement with the values on {101} faces values for the crystals in the literature [2]. The hardness of thoes higher borides are relatively higher than the values of REAlB₄ (RE = Tm, Yb, Lu) (TmAlB₄, 14.5 ± 1.4 GPa; YbAlB₄, 14.2 ± 1.4 GPa; LuAlB₄, 14.0 ± 0.6 GPa) or RE₂AlB₆ (RE = Lu, Sc) (Sc₂AlB₆, 12.7 ± 0.8 GPa; Lu₂AlB₆, 18.9 ± 0.7 GPa) [7, 9]. The values of the crystals obtained in the present work are appreciably higher than those measured of α-AlB₁₂ (21.4 ± 1.3 GPa) obtained in the binary Al-B system [10]. This nature of hardness seems to be related in the difference of B₁₂ icosahedral units and boron-boron networks built up (REAlB₄ and RE₂AlB₆) by five-, (add six-membered ring) and seven-membered rings for linkage of boron atoms in the structures, and in the number of B₁₂ icosahedral per unit area between the two-dimensional B₁₂ icosahedral networks.

The oxidation process of Al_xCu_yB₁₀₅ (x = 2.8–3.3, y = 2.9–1.0), Al_{1.3}Cu_{1.1}B₂₅ and CuB₂₃ crystals were studied by TG/DTA, and the results are shown in Fig. 2. The oxidation of Al_{1.1}Be_{0.7}B₂₂, Al_{1.4}Mg_{0.45}B₂₂, Al_{2.8}Cu_{2.9}B₁₀₅, Al_{3.1}Cu_{2.0}B₁₀₅, Al_{3.3}Cu_{1.0}B₁₀₅, Al_{1.3}Cu_{1.1}B₂₅ and CuB₂₃ crystals began to proceed at 1080, 1121, 746, 923, 984, 984 and 722 K, respectively. The weight gain of the compounds after TG determination are 77.0 mass% for Al_{1.1}Be_{0.7}B₂₂, 9.6 mass% for Al_{1.4}Mg_{0.45}B₂₂, in the range of 28.2 to 43.5 mass% for Al_xCu_yB₁₀₅ (x = 2.8–3.3, y = 2.9–1.0), 25.8 mass% for Al_{1.3}Cu_{1.1}B₂₅ and 61.4 maa% for CuB₂₃, respectively. The final oxidation phases were BeAl₂B₄, α-Al₂O₃, α-AlB₁₂, Cu₂O, CuO and B₂O₃, and so the exothermic peaks (see Table 5) are attributed to oxidation

products. However, the oxidation products of Al_{1.4}Mg_{0.45}B₂₂ were not detected from powder XRD, probably due to insufficient amount of these oxidation products. Data of the oxidation resistance of higher boride compounds (Al_{1.1}Be_{0.7}B₂₂, Al_{1.4}Mg_{0.45}B₂₂, Al_{2.8}Cu_{2.9}B₁₀₅, Al_{3.1}Cu_{2.0}B₁₀₅, Al_{3.3}Cu_{1.0}B₁₀₅, Al_{1.3}Cu_{1.1}B₂₅ and CuB₂₃) consisting of B₁₂ icosahedra have not been reported previously.

Recently, interesting magnetic behavior has been observed in B₁₂ icosahedral compounds like REB₂₂C₂N [8] and REB₅₀ [11]. It has been indicated that the magnetic interaction is mediated by the B₁₂ icosahedra [8, 11] which is a completely new phenomena in boride compounds. Therefore, it is important to characterize the magnetic properties of the new B₁₂ icosahedral Cu borides together with other related compounds, since the magnetic proper-

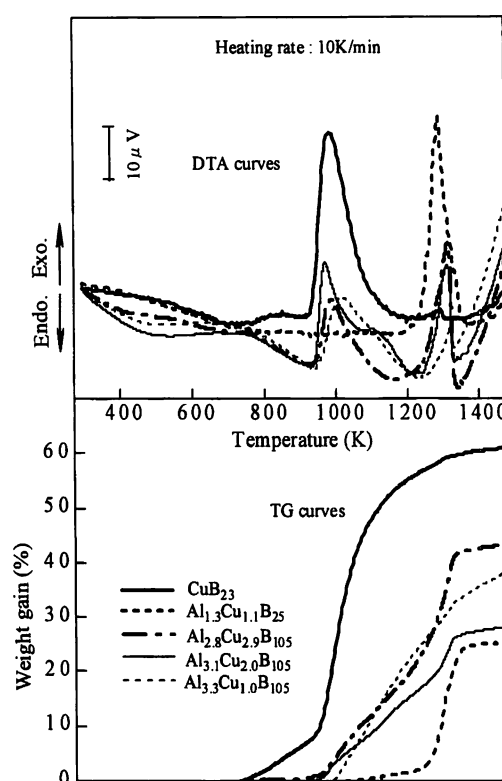


Fig. 2 TG/DTA curves for Al_xCu_yB₁₀₅ (x = 2.8–3.3, y = 2.9–1.0), Al_{1.3}Cu_{1.1}B₂₅ and CuB₂₃ crystals.

Table 4 Vickers microhardness of higher borides

Compound	Indentation Plane	Hardness (GPa)	Reference
Al _{1.1} Be _{0.7} B ₂₂	{101}	26.0(2.2)	This work
	{101}	23.9–28.2	[2]
Al _{1.4} Mg _{0.45} B ₂₂	{100}	25.4(0.5)	This work
Al _{2.8} Cu _{2.9} B ₁₀₅	{001}	27.2(1.8)	This work
Al _{3.1} Cu _{2.0} B ₁₀₅	{001}	27.8(1.7)	This work
Al _{3.3} Cu _{1.0} B ₁₀₅	{001}	27.6(2.7)	This work
Al _{1.3} Cu _{1.1} B ₂₅	{001}	26.3(2.3)	This work

Table 5 Results of the TG/DTA measurements for higher borides

Compound	Oxidation start (K)	Exothermic maximum (K)	Weight gain (mass%)	Oxidation products
Al _{1.1} Be _{0.7} B ₂₂	1082	1105, 1345	77.0	BeAl ₂ O ₄ , α-Al ₂ O ₃ , α-AlB ₁₂
Al _{1.4} Mg _{0.45} B ₂₂	1121	1121, 1421	9.6	—
Al _{2.8} Cu _{2.9} B ₁₀₅	746	976, 1307	43.5	α-Al ₂ O ₃ , Cu ₂ O, B ₂ O ₃
Al _{3.1} Cu _{2.0} B ₁₀₅	923	969, 1307	28.2	α-Al ₂ O ₃ , Cu ₂ O, B ₂ O ₃
Al _{3.3} Cu _{1.0} B ₁₀₅	984	1021, 1314	39.0	α-Al ₂ O ₃ , Cu ₂ O, B ₂ O ₃
Al _{1.3} Cu _{1.1} B ₂₅	984	1290	25.8	Cu ₂ O, CuO, B ₂ O ₃ , α-Al ₂ O ₃
CuB ₂₃	722	985	61.4	Cu ₂ O, B ₂ O ₃

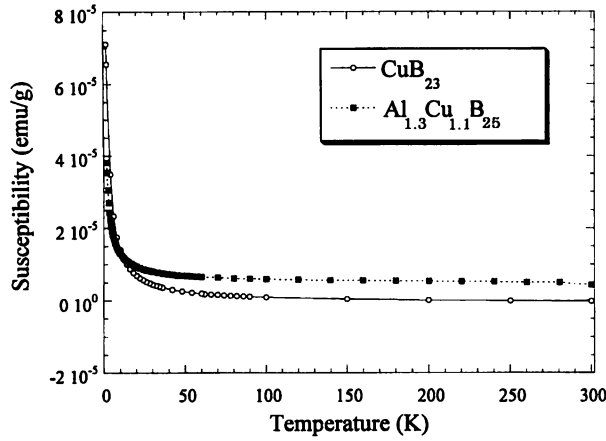


Fig. 3 Magnetic susceptibility of two Cu borides; CuB_{23} and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$.

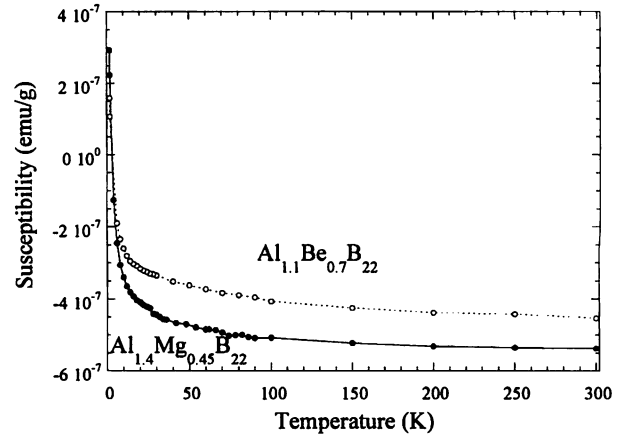


Fig. 5 Magnetic susceptibility of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ and $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$.

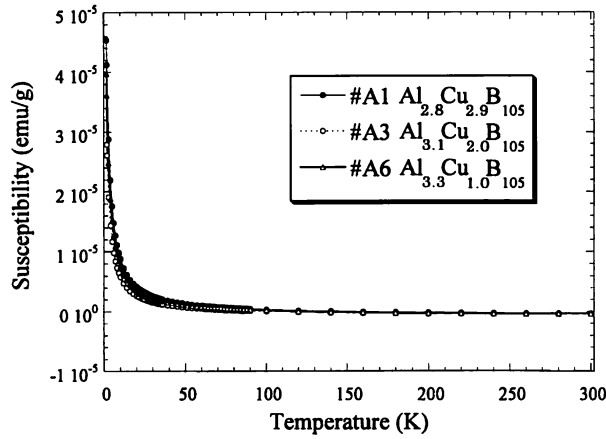


Fig. 4 Magnetic susceptibility of three $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) samples.

ties are completely unknown to date. The magnetic susceptibilities of all the borides measured in this work are shown in Figs. 3 to 5. In Figs. 3 and 4 we see that the Cu borides have a relatively strong paramagnetic contribution at low temperatures which indicates that there is contribution of magnetic moment from Cu. This is in contrast to $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ and $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ (Fig. 5), in which we observe a sizably smaller paramagnetic contribution indicating impurities or defects. This non-intrinsic low temperature paramagnetic tail has typically been observed for many of the higher borides [12]. None of the Cu borides show any anomalies at low temperatures down to 1.8 K indicative of a magnetic transition. Because of the presence of a non-intrinsic paramagnetic tail, we did not determine exact values for the effective magnetic moments of Cu.

In Fig. 4 we plotted the magnetic susceptibility of three $\text{Al}_x\text{Cu}_y\text{B}_{105}$ samples which were synthesized with slightly different crystal growth conditions. From the chemical analysis it is revealed that this causes a large difference in the stoichiometry. We can see that the susceptibility behavior of all the samples is similar and importantly, that

the base, i.e. the temperature independent part of susceptibility, takes a similar value regardless of the variations in stoichiometry of the metal elements. This result indicates that the compounds are non-metallic, which is reasonable considering the extremely boron-rich nature of the compounds. None of the compounds measured in this work are indicated to be superconducting down to 1.8 K.

4. Conclusion

1. $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$), $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ and CuB_{23} crystals were grown from high-temperature (1673 K or 1773 K) melts of the systems Al-M-B (M = Be, Mg, Cu) and Cu-B in an argon atmosphere.
2. The maximum dimensions of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were obtained in the ranges of approximately 2.5 to 5.2 mm. The $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ and $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ crystals were obtained as plate-like crystals having well-developed {101} and {001} faces, and $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals were obtained in the form of needle or rhombohedral plate as bounded by {001} faces and grew as prismatic shape extending in the c direction. CuB_{23} crystals had maximum dimensions of approximately 30 μm .
3. The values of Vickers microhardness on relatively large {101}, {100}, {001} and {001} faces of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) and $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ crystals are in the ranges of 25.4 (0.5) to 27.8 (1.7) GPa.
4. The oxidation of $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{2.8}\text{Cu}_{2.9}\text{B}_{105}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$, $\text{Al}_{3.3}\text{Cu}_{1.0}\text{B}_{105}$, $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ and CuB_{23} crystals began to proceed at 1080, 1121, 746, 923, 984, 984 and 722 K, respectively.
5. This result indicates that the compounds are non-metallic, which is reasonable considering the extremely boron-rich nature of the compounds. None of the compounds measured in this work are indicated to be superconducting down to 1.8 K.

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Al-ME-B (ME = Be, Mg, Cu) または Cu-B 系のメルトから 高ホウ化物の結晶育成と性質

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和文概要 アルゴンガス雰囲気中で Al-M-B (M = Be, Mg, Cu) 系および Cu-B 系の高温金属融剤から $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$), $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ および CuB_{23} 結晶を育成した。 $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ および $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ 結晶は 2.5~5.2 mm 程度の大きさである。しかし、 CuB_{23} 結晶は約 30 μm の大きさであった。 $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$ と $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$ 結晶はよく発達した {101} と {001} 面を有した板状結晶で、 $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$ と $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ 結晶は {001} 面に囲まれた針状または菱面体状の板状或いは c 軸方向に成長した棒状結晶で得られる。{101}, {100}, {001} と {001} 上で測定した $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_x\text{Cu}_y\text{B}_{105}$ ($x = 2.8 - 3.3$, $y = 2.9 - 1.0$) および $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ 結晶のビッカース微小硬さは 25.4 (0.5)~27.8 (1.7) GPa の範囲内である。TG 曲線から $\text{Al}_{1.1}\text{Be}_{0.7}\text{B}_{22}$, $\text{Al}_{1.4}\text{Mg}_{0.45}\text{B}_{22}$, $\text{Al}_{2.8}\text{Cu}_{2.9}\text{B}_{105}$, $\text{Al}_{3.1}\text{Cu}_{2.0}\text{B}_{105}$, $\text{Al}_{3.3}\text{Cu}_{1.0}\text{B}_{105}$, $\text{Al}_{1.3}\text{Cu}_{1.1}\text{B}_{25}$ と CuB_{23} の酸化開始はそれぞれ 1080, 1121, 746, 923, 984, 984 と 722 K である。各化合物とも異常な磁化率挙動を示さなく、異なった組成比を有する三種類の $\text{Al}_x\text{Cu}_y\text{B}_{105}$ 化合物は温度に依存した磁化を示し、非金属的な振る舞いをしている。これら化合物は室温 (300 K) から 1.8 K までの温度では超伝導体特性を示さない。