Original Paper

Crystal Growth and Some Properties of α-$REAlB_4$ Type (RE = Ho, Er, Tm, Yb and Lu) Compounds

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The crystals of α-$REAlB_4$ type (orthorhombic, *Pbam*) (RE = Ho, Er, Tm, Yb and Lu) compounds were grown from the RE-Al-B system using a molten Al-self flux kept at 1873 K for 5 h under an argon atmosphere. The as-grown α-$REAlB_4$ type crystals were subjected to phase analysis and measurements of lattice parameters. The present study of the new compound $HoAlB_4$ is the first crystal growth study. The α-$REAlB_4$ crystals were obtained in the form of plate- or needle-like prisms and were having a grayish color. The micro-Vickers hardness values of α-$REAlB_4$ crystals were in the range of 16.8-18.5 GPa. The magnetic susceptibility of powder crystalline samples of α-$YbAlB_4$, α-$ErAlB_4$, and α-$HoAlB_4$ were measured using a SQUID magnetometer. Antiferromagnetic transitions were observed for α-$HoAlB_4$ and α-$ErAlB_4$ crystals at T_N = 4.5 K and T_N = 5.0 K, respectively. The magnetic susceptibility of our powdered α-$YbAlB_4$ crystals showed a larger low temperature paramagnetic tail compared to previous reports, and may be due to defects.

Key Words: *α-$REAlB_4$ Type Compounds*, *Lattice Parameter*, *Micro-Vickers Hardness*, *Magnetic Susceptibility*

1. Introduction

In the ternary RE-Al-B systems (RE = rare earth), four main types of ternary crystal structures have been reported, namely the $YCrB_4$ type (so-called α-$REAlB_4$ type, orthorhombic, space group: *Pbam*)[1-3], the $ThMoB_4$ type (β-$REAlB_4$ type, orthorhombic, space group: *Cmmm*)[4], the Y_2ReB_6 type (Yb_2AlB_6, orthorhombic, space group: *Pbam*)[1,3] and the $MgAlB_{14}$ type ($REAlB_{14}$ with RE = Tb, Dy, Ho, Er, orthorhombic, space group: *Imma*)[5]. Recently, in the ternary Tm-Al-B system, the β-$TmAlB_4$ compound[6] and Tm_2AlB_6 compound[7] were reported to be synthesized for the first time, and exhibited interesting magnetic properties. The crystal structure of the $YCrB_4$-type (and the $ThMoB_4$-type) has an analogy to that of the AlB_2 type compounds and also the REB_4 type compounds with three bonded boron atoms forming a network of planar five- and seven-membered rings to accommodate the differently sized rare earth and aluminum atoms in between the boron planes. The crystal structures of the α-$REAlB_4$ and β-$TmAlB_4$ compounds were shown in Fig.1 and Fig.2 (Small and medium sized circles, respectively, indicate boron and aluminum atoms. Filled large circles indicate the RE atoms). α-$TmAlB_4$ exhibits an antiferromagnetic transition at T_N = 5.8 K[8] and showed interesting additional anomalies indicated to originate from building defects[9]. The hardness values of $TmAlB_4$, $YbAlB_4$ and $LuAlB_4$ crystals of $YCrB_4$ type compound were in the range of 14.0(0.6)-14.5(1.4) GPa[3]. However, there is still relatively little systematic information about the physical and chemical properties of the rare earth series of α-$REAlB_4$ type compound. In this work, we report the experimental conditions for growing relatively large crystals of α-$REAlB_4$ (RE = Ho, Er, Tm, Yb and Lu) from rare earth metals (Ho, Er, Tm, Yb and Lu) and boron powders as starting materials using Al-self flux. The present study of the new compound $HoAlB_4$ is the first crystal growth study. The morphology and crystallographic data of the α-$REAlB_4$ crystals were determined and also micro-Vickers hardness at room

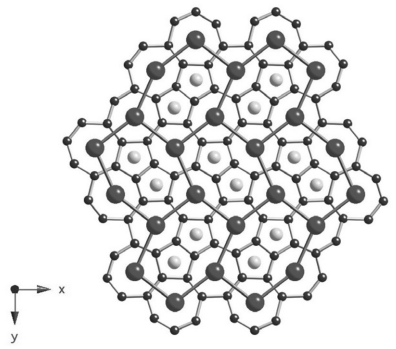


Fig.1 The crystal structure of the α-$REAlB_4$.

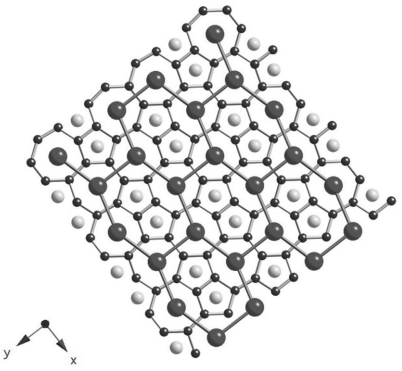


Fig.2 The crystal structure of the β-$TmAlB_4$.

temperature and magnetic susceptibility were measured.

2. Experiment

The reagents used to prepare the samples were rare earth metals (Ho, Er, Tm, Yb and Lu) (purity 99-99.9 %), crystalline boron (purity 99 %) and Al metal chips (purity 99.99 %). The growth conditions for $REAlB_4$ were established using the starting mixtures of the atomic ratio n = B/RE = 4.0. Al metal was added to each mixture at mass ratio of 1:15-20. The crucible was inserted in a vertical electric furnace with a SiC heater, and heated in an argon atmosphere. The mixture was heated at a rate of 300 $K \cdot h^{-1}$ and kept at 1873 K for 5 h. The solution was cooled to 1273 K at a rate of 50 $K \cdot h^{-1}$ and then the furnace was switched off. The crystals were removed from the solidified melt by dissolving the matrix in 6 mol hydrochloric acid. Phase analyses and determination of lattice parameters were carried out using a powder X-ray diffractometer (XRD) (Rigaku Co., RINT-2000) with monochromated Cu $K\alpha$ radiation. The chemical compositions and impurities of the grown crystals were evaluated by means of energy dispersive spectroscopy (EDS) (KEYENCE Co., PV-7750/75ME). The morphology and size of the as-grown crystals were examined in a stereomicroscope and a scanning electron microscope (SEM) (KEYENCE Co., VE-7800). Measurements on the as-grown α-$REAlB_4$ (RE = Ho, Er, Tm, Yb and Lu) crystals were done using a Vickers diamond indenter at room temperature. A load of 1.96 N was applied for 15 s at about five positions on relatively large faces of each crystal. The magnetic susceptibility of powdered samples of α-$YbAlB_4$, α-$ErAlB_4$, and α-$HoAlB_4$ crystals were measured in a magnetic field of 100 mT using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 300 K to 1.8 K.

3. Results and Discussion

The crystals of α-$REAlB_4$ type compound were grown from the high-temperature solution Al-self flux in an argon atmosphere. Figure 3 shows XRD patterns of α-$REAlB_4$ type crystals. Almost all diffraction peaks of the obtained α-$REAlB_4$ crystals are fitted to the space group *Pbam* which is as same as that of $YCrB_4$ type structure. However, it should be noted that α-$REAlB_4$ crystals were obtained together with tetraborides REB_4 or hexaborides REB_6 or Lu_2AlB_6 crystals in the case of the lutetium sample. α-$REAlB_4$ crystals were selected from the other borides by using a stereomicroscope. At the same time, crystals of REB_2, Tm_2AlB_6, α-AlB_{12}, γ-AlB_{12}, REB_{12}, $TmAlB_{14}$ and REB_{66} were not detected by powder XRD. α-$REAlB_4$ crystals were obtained in the form of plate- or needle-like prisms and were having a grayish color. Figure 4 indicated SEM photographs of $HoAlB_4$ and $ErAlB_4$ crystals. The crystals have maximum dimensions of approximately 4.5 mm. A well characterized ternary metal boride Ho-Al-B compound has so far not been reported. The diffraction data for α-$HoAlB_4$ are very similar to those reported for α-$TmAlB_4$ {a = 0.59175(6) nm, b = 1.1472(1) nm, c = 0.34773(3) nm}[2], α-$YbAlB_4$ {a = 0.5919(1) nm, b = 1.1465(2) nm, c = 0.3492(1) nm}[3] and α-$LuAlB_4$ {a = 0.5906(2) nm, b = 1.144(1) nm, c = 0.3480(1) nm}[1]. The results of determination of the lattice parameters for as-grown α-$REAlB_4$ crystals are listed in Table 1 together with the reference values.

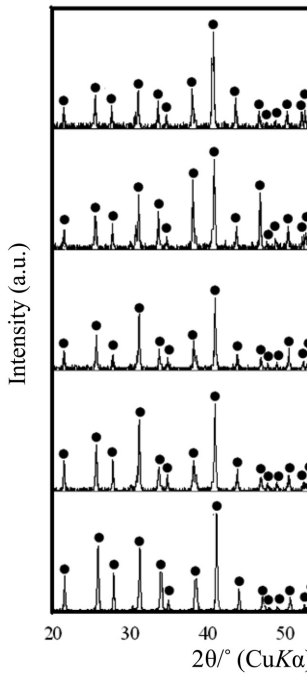
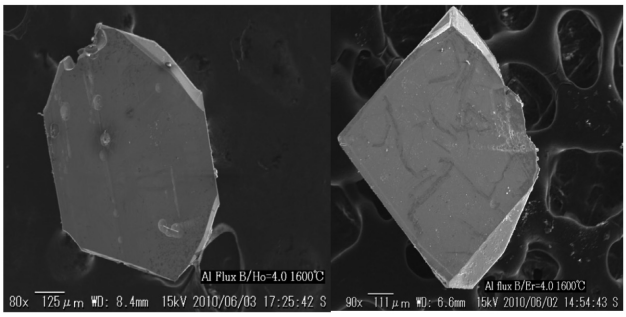


Fig.3 The XRD patterns of α-$REAlB_4$ type compounds.



$HoAlB_4$ **$ErAlB_4$**

Fig.4 SEM photographs of $HoAlB_4$ and $ErAlB_4$ crystals.

The micro-Vickers hardness for crystals of α-$REAlB_4$ type was measured in several directions on the {100} or {001} faces. The hardness values of α-$REAlB_4$ crystals for the holmium and erbium phases were in the range of 16.8-18.5 GPa. These values are in relatively good agreement with the values published in the literature {$TmAlB_4$: 14.5(1.4) GPa, $YbAlB_4$: 14.2(1.4) GPa, $LuAlB_4$: 14.0(0.6) GPa}[2,3]. However, despite the error bar, we can conclude that there appears to be a trend that the α-$REAlB_4$ holmium and erbium crystals have higher hardness values than the thulium, ytterbium, and lutetium crystals. The hardness values of α-$REAlB_4$ crystals were relatively lower than the value of REB_4 (HoB_4: 23.3 GPa, ErB_4: 24.9 GPa, TmB_4: 20.9 GPa, YbB_4: 22.3 GPa, LuB_4: 19.2 GPa), REB_6 (YbB_6: 21.9 GPa) and dodecaborides REB_{12} (HoB_{12}: 26.5 GPa, ErB_{12}: 27.5 GPa, TmB_{12}: 29.4 GPa, YbB_{12}: 32.4 GPa, LuB_{12}: 28.4 GPa)[10,11]. This nature of hardness seems to be related in the difference for latter compounds which have boron clusters of octahedron B_4 or B_6 and cubo-octahedron B_{12} built up by linkage of boron-boron atoms, compared to the alternating boron and metal 2D atomic sheets of the α-$REAlB_4$ compounds. Investigation into the magnetism of rare earth borides like REB_4, REB_6, and REB_{12} has yielded interesting results over the years[12-14]. Striking magnetic behavior has also been observed in boron-richer borides which contain the B_{12} icosahedra as a structural building block. A wide variation of magnetism has been discovered ranging from one-dimensional dimer-like magnetic transitions in REB_{50} and $REB_{44}Si_2$[15], two-dimensional spin-glass behavior in $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$[16] to three-dimensional long-range order in $GdB_{18}Si_5$. Although these are magnetically dilute *f*-electron insulators, surprisingly strong magnetic coupling has been observed (e.g., T_N = 17 K for TbB_{50}[15], peak of ZFC susceptibility T_f = 29 K for $HoB_{17}CN$[16]).

Table 1 Lattice parameters of as-grown α-$REAlB_4$ crystals.

Compounds	Structure Type	Lattice parameters / nm *a*	*b*	*c*	Ref.
α-$HoAlB_4$	$YCrB_4$	0.5931(4)	1.1485(6)	0.3481(4)	This work
α-$ErAlB_4$	$YCrB_4$	0.5918(3)	1.1457(4)	0.3477(6)	This work
α-$TmAlB_4$		0.5889(4)	1.1401(9)	0.3441(7)	This work
	$YCrB_4$ (α-phase)	0.5918(1)	1.1472(1)	0.3477(1)	[2]
	$YCrB_4$	0.59225(2)	1.14784(5)	0.35224(2)	[9]
	$ThMoB_4$ (β-phase)	0.72795(6)	0.93248(8)	0.37981(3)	[17]
α-$YbAlB_4$	$YCrB_4$	0.5915(4)	1.1455(6)	0.3468(6)	This work
		0.5927(2)	1.147(1)	0.3492(1)	[1]
		0.5919(1)	1.1465(2)	0.3492(1)	[2]
α-$LuAlB_4$	$YCrB_4$	0.5889(6)	1.1418(8)	0.3442(9)	This work
		0.5906(2)	1.144(1)	0.3480(1)	[1]
		0.5898(1)	1.1440(1)	0.3485(1)	[2]

The rare earth metal aluminoboride system $REAlB_4$ has also been attracting increasing attention with recent discoveries. Multiple magnetic transitions were reported to occur at low temperatures below the antiferromagnetic transition temperature T_N in the $YCrB_4$ type structure compound $TmAlB_4$[8]. The origin of this behavior was discovered to be due to an intrinsic tiling variation (building defects) in the crystals[9]. This tiling variation is indicated to occur due to the presence of the closely related $ThMoB_4$ type structure described above. The existence of building defects has been directly observed by TEM[17]. The difference between the $YCrB_4$ type and $ThMoB_4$ type structures is in the orientation of the pairs of condensed pentagonal rings, i.e., tiling. In this work, we have measured the magnetic susceptibility of powder crystalline samples of α-$YbAlB_4$, α-$ErAlB_4$ and α-$HoAlB_4$. The results obtained for α-$HoAlB_4$ and α-$ErAlB_4$ are plotted in Fig.5. As can be seen, an antiferromagnetic transition is observed at T_N = 4.5 K and T_N = 5.0 K for α-$HoAlB_4$ and α-$ErAlB_4$, respectively. The difference in the magnitude of the magnetic susceptibility of α-$HoAlB_4$ and α-$ErAlB_4$ is due to the difference in magnitude of the magnetic moments of holmium and erbium ions. Previously the magnetism of β-$ErAlB_4$[18] was investigated and an antiferromagnetic transition was observed at T_N = 4.3 K which is a little lower than that observed for α-$ErAlB_4$ here. This trend is interesting since it was found for the thulium phase that the β-phase has a significantly (60 %) higher transition temperature than the α-phase[6]. This magnetic behavior will be investigated in more detail in other works. The magnetic susceptibility of powder crystalline α-$YbAlB_4$ is shown in Fig.6. Magnetic transitions are not observed and the results are consistent with the results previously obtained for a single crystalline sample[19]. However, we note that our low

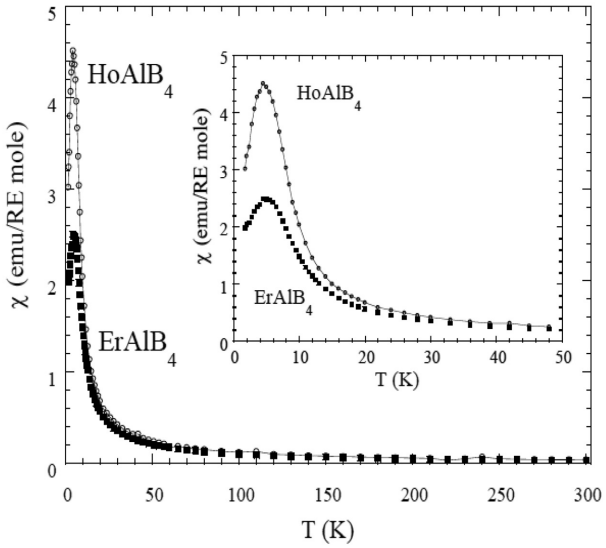


Fig.5 Magnetic susceptibility of α-$ErAlB_4$ and α-$HoAlB_4$ crystals.

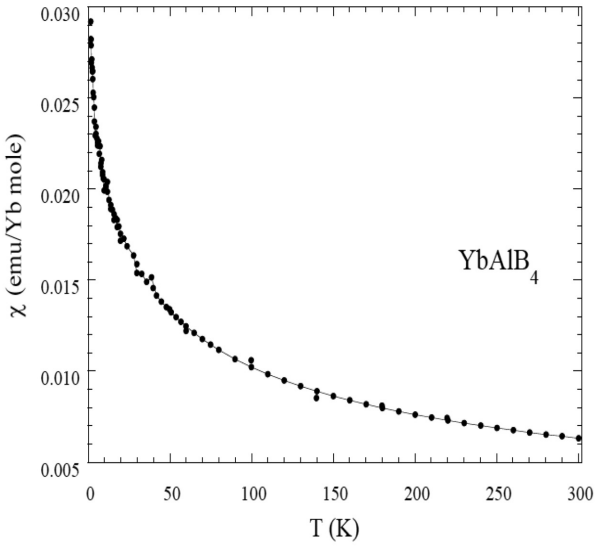


Fig.6 Magnetic susceptibility of α-$YbAlB_4$ crystal.

temperature tail is larger which can be explained by an increase in defects in our sample compared to the single crystal sample. The magnitude of the magnetic susceptibility of α-$YbAlB_4$ is very small compared to the holmium and erbium phases and it is indicated there is valence instability of ytterbium.

4. Conclusions

The crystals of α-$REAlB_4$ type (orthorhombic, *Pbam*) (RE = Ho, Er, Tm, Yb and Lu) compounds were grown by the RE-Al-B system using a molten Al-self flux kept at 1873 K for 5 h under an argon atmosphere. The α-$REAlB_4$ crystals were obtained together with REB_4 or REB_6 or Lu_2AlB_6 crystals. The present study of the new compound $HoAlB_4$ is the first crystal growth study. The morphology and crystallographic data of the crystals were determined, and micro-Vickers hardness at room temperature and magnetic susceptibility from 300 K to 1.8 K were measured. The results are as follows.

(1) α-$REAlB_4$ crystals were obtained in the form of plate- or needle-like prisms and were having grayish color. The crystals have maximum dimensions of approximately 4.5 mm.
(2) The hardness values of α-$REAlB_4$ crystals for Ho and Er phases were in the range of 16.8-18.5 GPa, which is larger than that of 13.4-15.9 GPa for Tm, Yb, and Lu phases.
(3) The magnetic susceptibility of α-$HoAlB_4$ and α-$ErAlB_4$ are observed for antiferromagnetic transition at T_N = 4.5 K and T_N = 5.0 K, respectively. The magnetic susceptibility of α-$YbAlB_4$ has a low temperature tail larger than that previous observed for single crystal samples which can be due to a larger number of defects in our α-$YbAlB_4$ samples.

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