JOURNAL OF SOLID STATE CHEMISTRY **133,** 55–58 (1997)
ARTICLE NO. SC977317

Single Crystal Growth of a New YB_{50} Family Compound: $YB_{44}Si_{1.0}$

Takaho Tanaka, Shigeru Okada,* and Yoshio Ishizawa

*National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan; and *Department of Applied Chemistry, Kanagawa University, Yokohama, Kanagawa 221, Japan*

Received January 16, 1997; accepted February 6, 1997

Single crystals of a new yttrium borosilicide of $YB_{44}Si_{1.0}$ have been grown by the floating zone method using a xenon lamp image furnace. X-ray powder diffraction, precession photography, and chemical analyses showed that the crystal obtained is a new YB_{50} family yttrium borosilicide which has a composition of $YB_{44.4}Si_{1.04}$ in the middle part of the crystal and an orthorhombic crystal structure with space group *Pbam* or *Pba2*.

INTRODUCTION

It has been reported that two new phases exist between the previously known phases of YB_{12} and YB_{66} [1] with compositions of about $[B]/[Y] = 25$ and 50, respectively. These values suggest that the crystal structures of both boron-rich borides are built up of boron icosahedra. For crystal chemistry purposes, growth of crystal grains is sufficient for structural analysis of these new borides. But, because of potential applications, it is more and more important to grow sizable single crystals of these new borides in order to search for novel functional properties.

A single phase was established at around $[B]/[Y] = 50$ for the phase richer in boron. X-ray powder diffraction and electron diffraction analyses for a powder sample showed that YB_{50} has an orthorhombic crystal structure with lattice constants $a = 1.66251(9)$ nm, $b = 1.76198(11)$ nm, and $c = 0.94797(3)$ nm [1]. The space group of YB_{50} was previously proposed to be $P2_12_12$ [1], which is corrected in the present work. These results suggested that YB_{50} can be classified as a structural type similar to γ-AlB_{12}, because γ-AlB_{12} has an orthorhombic structure with very similar lattice constants of $a = 1.6573(4)$, $b = 1.7510(3)$, $c = 1.0144(1)$ nm, and space group $P2_12_12_1$ [2].

It was expected that reduction of metal atom content from γ-AlB_{12} modified the bonding scheme between boron icosahedra along the c-axis, decreasing the c-axis and changing the extinction rule from even l for $00l$ of γ-AlB_{12} to no l condition in YB_{50}.

In the present paper, we report the single crystal growth of a new yttrium borosilicide of $YB_{44}Si_{1.0}$ which is a family compound of YB_{50}. We present a variation of the melt growth method, where the addition of a third element (Si) enables coexistence of the YB_{50} phase with the melt, resulting in successful crystal growth by the floating zone method.

EXPERIMENTAL

Preparation of polycrystalline rod. Polycrystalline rods for the floating zone method were prepared by arc-melting. Powders of YB_4, amorphous boron, and Si were weighed to give the desired composition. They were thoroughly mixed in an agate mortar with ethanol. The mixed powder was pressed into a green rod by a CIP process at 2,500 kg/cm^2. The green rod was arc-melted in a semicircular groove on a water cooled copper plate under Ar gas atmosphere. The arc-melted rod was about 6 mm in diameter and 100 mm long. In order to obtain uniform diameter and uniform composition distribution, the arc-melting was repeated, changing the sweep direction of the arc. A small pellet which was used for the molten zone in the floating zone crystal growth was also made by the arc-melting method.

Floating zone crystal growth. Floating zone crystal growth was carried out using a xenon lamp image furnace under flowing argon. Despite the careful preparation of the feed rod by the arc-melting mentioned above, the diameter and also the composition distribution of the feed rod were not sufficiently uniform. This required a double zone pass. In the first zone pass, with a high driving rate of about 30 mm/h, the feed rate was constantly adjusted to obtain a uniform diameter. The first zone pass was also effective in reducing the composition fluctuation of the feed rod. In the second zone pass, the zone pass direction was reversed relative to the first pass. The initial molten zone for the second pass was formed by remelting the molten zone frozen after the first zone pass. Both the feed rod and the growing crystal were synchronously driven downward at 10 mm/h and counter-rotated at 30 rpm.

0022-4596/97 $25.00

Characterization of the crystals. The crystals obtained were characterized by both X-ray powder diffraction and chemical analysis. Seed end, middle, and zone end parts of the crystals and the molten zone were pulverized using a stainless steel mortar. The stainless steel contamination was removed by dissolving in a hydrochloric acid solution, decanting and rinsing. The X-ray powder diffraction measurements were carried out using a standard X-ray powder diffractometer after the coarse powder was pulverized to a fine powder using an agate mortar.

Yttrium, silicon, and boron content were determined by inductively coupled plasma atomic emission spectroscopy (ICP) after the coarse powder was dissolved into conc. HNO_3 + conc.HCl (1:1) solution at 110°C for about 12 h.

Precession photography was carried out using a standard precession camera (Enraf Nonius) and Cu$K\alpha$-radiation because of the relatively large lattice constants.

RESULTS AND DISCUSSION

The YB_{50} phase starts to decompose into YB_{25} and YB_{66} at 1700°C without melting. This makes single crystal melt growth of YB_{50} difficult. It may be possible to obtain a crystal grain, suitable for single crystal X-ray diffraction analysis, by a high temperature solution growth method. However, saturation boron content is usually low in the metal fluxes which are commonly used for boride growth, such as Al, Sn, and Sb. It is not particularly easy to grow a single crystal of higher borides such as YB_{50} using such a method.

It is inconvenient to use Al flux because of the difficulty of distinguishing whether the crystals obtained are YB_{50} or γ-AlB_{12}, although Al flux is most popular for the high temperature solution growth of borides. Sn and Sb fluxes were unsuccessful. Transition metal borides such as CoB and NiB have relatively low melting temperature and high boron content. They may be usable as a flux agent for high temperature solution growth of YB_{50}. Both CoB and NiB were tried and single crystals of size 1–2 mm size were obtained. X-ray powder diffraction patterns of those crystals were the same as that of YB_{50}. However, electron probe microanalysis showed that those crystals contained a considerable amount of Co or Ni. For example, a crystal grown from the NiB melt showed a [Y]/[Ni] ratio of 0.8/0.2. Moreover, the crystal size was insufficient for physical property measurements.

The melt growth method is most suitable for growing a large crystal. One possible improvement of the melt growth method is to add a third element to stabilize the YB_{50} phase and enable it to coexist with the melt. In fact, such a method has been applied to the crystal growth of WC, which, like YB_{50}, decomposes into solid state compounds at elevated temperatures. WC single crystals were successfully grown using the floating zone method by adding boron as a stabilizing agent [3]. In the WC case standards for searching for the third element were; (1) the third element should form a stable compound with a dominant constituent element of the original compound, (2) the crystal structure of the compound should resemble that of the original compound, and (3) the compound should melt.

In the case of YB_{50}, carbon and silicon may be candidates for the third element as they seem to satisfy to some extent the standards mentioned above. Boron, which must be the dominant element in boron-rich borides, forms stable B_4C-type compounds with carbon and silicon which melt congruently. At the present stage, no one knows how similar the crystal structures of B_4C and YB_{50} are. There is no doubt that the basic structural unit of both crystal structures is the boron icosahedron.

As a preliminary experiment, YB_{50} was arc-melted while carbon and/or silicon was added to examine whether carbon or silicon could be the third element for YB_{50}. Carbon addition only decomposed YB_{50} into YB_4 and B_4C. On the other hand, silicon addition formed a compound which showed the same X-ray diffraction pattern as that of YB_{50}. Nominal compositions from $YB_{50}Si_{10}$ to $YB_{50}Si_3$ could form the YB_{50} family compound. After further reduction of silicon the YB_{66} phase appeared instead of the YB_{50} family compound.

The arc-melted sample of $YB_{50}Si_3$ was not a single phase but consisted of the YB_{50} family compound and free silicon. This result showed that silicon content in the YB_{50} family compound is less than $YB_{50}Si_3$ and that the compound could be grown from the melt of $YB_{50}Si_3$. As was shown by several zone pass trials for feed rods with different compositions and chemical analyses, the YB_{50} family compound with composition of about $YB_{45}Si_{1.0}$ can be grown from the melt of $YB_{40}Si_3$.

Rods having nominal composition $YB_{45}Si_{1.8}$ were prepared for both the feed rod and the seed rod of the floating zone crystal growth. A tip, of composition $YB_{40}Si_{3.5}$, was inserted between the feed rod and the seed rod and was melted to form the initial molten zone. The difference between the nominal composition and the actual composition after zone melting is due to the ignition losses of raw powders of YB_4, Si, and amorphous B.

An example of the crystals obtained is shown in Fig. 1(a). The crystal is about 8 mm in diameter and 50 mm long. The observation for cross sections of the crystal showed occurrences of sub-grains and cracks. The X-ray diffraction patterns of various parts of the crystal were the same as those of YB_{50}. A typical diffraction pattern of the crystal is compared with that of YB_{50} in Fig. 1(b). Both diffraction patterns are similar though lattice constants of $YB_{44}Si_{1.0}$ are slightly shorter than those of YB_{50} and the intensity relation between diffraction peaks of $YB_{44}Si_{1.0}$ is partly different from that of YB_{50}. Thus the crystal obtained is a new

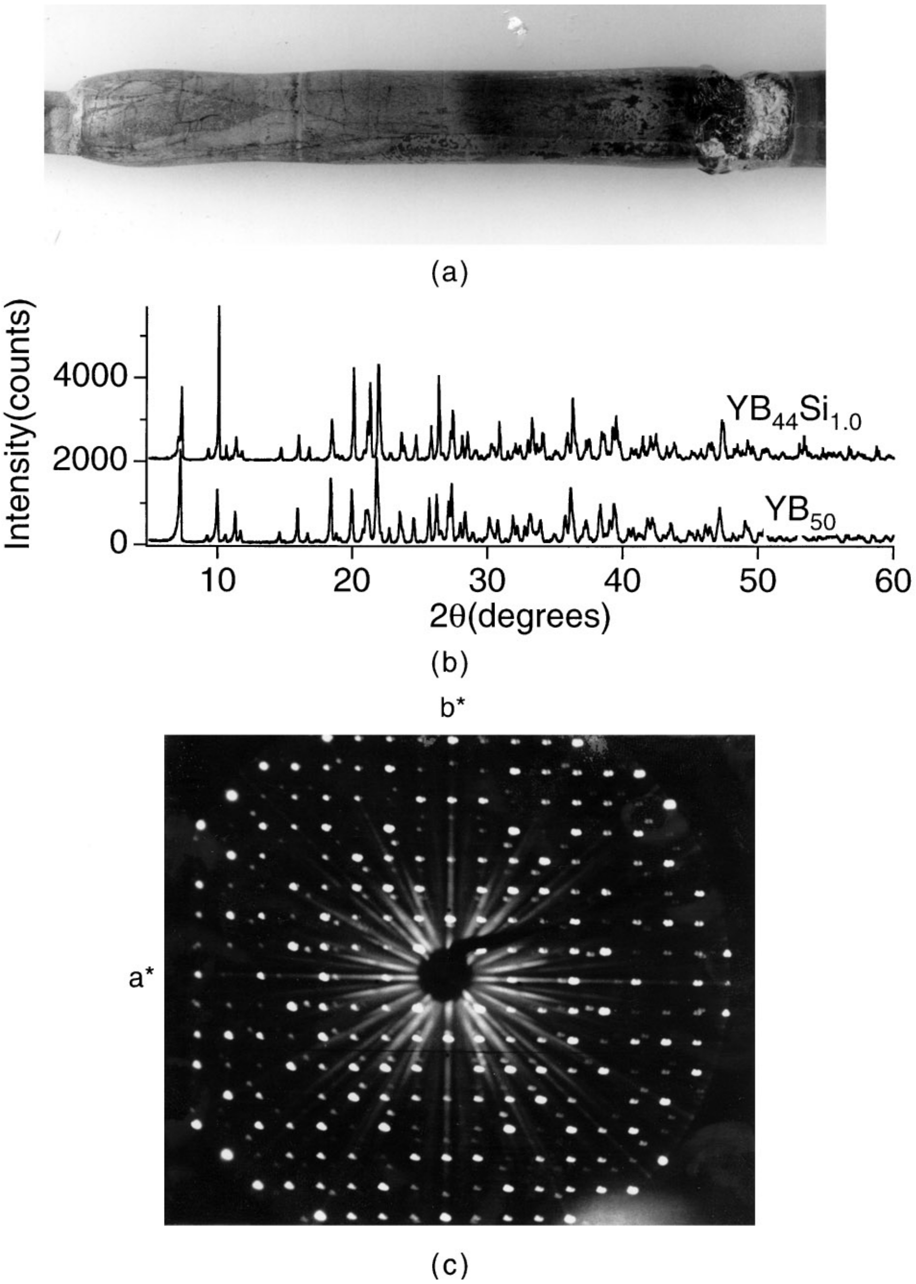

FIG. 1. (a) Single crystal of $YB_{44}Si_{1.0}$, (b) x-ray powder diffraction patterns of $YB_{44}Si_{1.0}$ and YB_{50}, and (c) precession photograph of *hk*0 plane.

yttrium borosilicide crystal of $YB_{44}Si_{1.0}$ which is a YB_{50} family compound. The chemical compositions of the crystal are summarized in Table 1. The partition coefficient of Si is about 0.5.

The chemical analysis showed that the molten zone contained about 7 wt% of copper impurity, which is not listed in Table 1. However, the copper content in the crystal was relatively low, less than 0.5 wt%. The partition coefficient of copper impurity is less than 0.1. Molten yttrium borosilicide has low electrical conductivity compared with metals. Thus the arc often discharges not to the sample but to the copper plate during the feed rod preparation process. Moreover, the molten yttrium borosilicide in the groove tends to assume a droplet form rather than a rod form. All these factors make it difficult to prepare a raw polycrystalline rod by the arc-melting method. Multiple arc-melting was necessary, resulting in incorporation of the copper impurity. The temperature of the molten zone during floating zone growth exceeds 2000°C, and so considerable amount of copper evaporated from the molten zone. Nevertheless, a sizable

TABLE 1
Chemical Composition of the $YB_{44}Si_{1.0}$ Crystal

Position	Composition
Feed rod	$YB_{41.6}Si_{1.45}$
Middle(cry.)	$YB_{44.4}Si_{1.04}$
End(cry.)	$YB_{44.3}Si_{1.27}$
Zone	$YB_{41.5}Si_{2.82}$

TABLE 2
Extinction Rules of the $YB_{44}Si_{1.0}$ Crystal Determined by Precession Photography

*h*00:	*h* = 2n
0*k*0:	*k* = 2n
00*l*:	*l* = no condition
hkl:	no condition
*hk*l:	no condition
*h*0l:	*h* = 2*n*
0*k*1:	*k* = 2*n*
0*kl*:	*k* = 2*n*
1*kl*:	no condition
1*k*0:	no condition

Note. Expected space group: *Pbam*, *Pba*2.

amount of copper impurity remained in the molten zone. Fortunately, the copper content in the crystal was low because of the low partition coefficient of copper. However, the high evaporation rate and the high concentration of the copper impurity in the molten zone seem to cause instability of the molten zone, which causes the cracks in the crystal.

Single crystal precession photography was carried out in order to examine the diffraction rules of $YB_{44}Si_{1.0}$. Precession photographs of the *hk*0, 0*kl*, *hk*1, and 1*kl* planes were taken. As an example, the *hk*0 plane photograph is shown in Fig. 1(c). The extinction rules obtained, which are summarized in Table 2, indicate that the space group of this new yttrium borosilicide is *Pbam* or *Pba*2.

The space group of YB_{50} was previously proposed to be $P2_12_12$ [1]. However, it was confirmed by reexamining fully indexed powder diffraction data from YB_{50} that YB_{50} also satisfies the same extinction rule as $YB_{44}Si_{1.0}$. The space group of YB_{50} is also *Pbam* or *Pba*2.

Is it possible to propose a crystal structure of $YB_{44}Si_{1.0}$ based on the γ-AlB_{12} type structure because the lattice constants of both structures are similar, as mentioned above? Probably not, as modifications of the γ-AlB_{12} type structure cannot form a crystal structure whose space group is *Pbam* or *Pba*2 [4]. This means that YB_{50} and $YB_{44}Si_{1.0}$ should be classified into the same new structure type, which is different from the γ-AlB_{12} type structure. The structure analysis with a four-circle diffractometer showed that $YB_{44}Si_{1.0}$ has an orthorhombic structure ($YB_{43.5}Si_2$, space group *Pbam*, $a = 1.6674(1)$ nm, $b = 1.7667(1)$ nm, and $c = 0.95110(7)$ nm). Details will be presented elsewhere [5].

CONCLUSION

Single crystals of a new yttrium borosilicide of $YB_{44}Si_{1.0}$ have been grown by the floating zone method using a xenon lamp image furnace. At the present stage, the quality of the crystal obtained was not so high because of relatively high concentration of copper impurity in the raw polycrystalline feed rod prepared by the arc-melting method. X-ray powder diffraction and chemical analyses showed that the crystal is a new YB_{50} family yttrium borosilicide which has a composition of $YB_{44.4}Si_{1.04}$ in the middle part of the crystal. The crystal structure of this new yttrium borosilicide is orthorhombic with space group *Pbam* and the lattice constants $a = 1.6674(1)$ nm, $b = 1.7667(1)$ nm, and $c = 0.95110(7)$ nm.

REFERENCES

1. T. Tanaka, S. Okada, and Y. Ishizawa, *J. Alloys Comp.* **205,** 281 (1994).
2. I. Higashi, *J. Solid State Chem.* **47,** 333 (1983).
3. T. Tanaka, S. Otani, and Y. Ishizawa, *J. Mater. Sci.* **23,** 665 (1988).
4. I. Higashi, private communication.
5. I. Higashi, T. Tanaka, K. Kobayashi, Y. Ishizawa, and M. Takami, *J. Solid State Chem.* **133,** 11 (1997).