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A New Yttrium Boride: YB_{25}

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A new yttrium boride has been found to exist between YB_{12} and YB_{50}. A single phase was established at a nominal composition of [B]/[Y] = 25.5–26.0. X ray powder diffraction and electron diffraction analyses showed that the new YB_{25} phase has a monoclinic system with $a = 0.82842(3)$ nm, $b = 1.03203(3)$ nm, $c = 0.58570(2)$ nm, $\beta = 90.402(3)^\circ$, and space group $I121$(No. 5), $I1m1$ (No. 8), or $I12/m1$ (No. 12). Rare earth elements from Gd to Ho can also form compounds isostructural to YB_{25}. © 1997 **Academic Press**

INTRODUCTION

It has been thought that the binary phase diagram of the yttrium–boron system is well established (1). The last discovery in the Y–B system was cubic YB_{66}, found by Seybolt (2) in 1960; its structure was determined by Richards and Kasper (3) in 1969. Recently, however, one of the present authors (T. Tanaka) found two unknown intermediate phases between YB_{12} and YB_{66} during his crystal growth work in YB_{66} (4, 5). For the boron richer phase of the two unknown phases, the single phase was rather easily established at around [B]/[Y] = 50. The crystal structure of YB_{50} was determined to be orthorhombic with $a = 1.6625$ nm, $b = 1.7620$ nm, and $c = 0.94797$ nm (5).

On the other hand, it took some time to establish a single phase with composition around [B]/[Y] = 25. After several careful experiments, it was found that single phases of YB_{25} appeared at mixing ratios of [B]/[Y] = 25.5–26.0. The single phase compound obtained was investigated by powder X ray diffraction and electron diffraction analyses to determine the cell dimensions and extinction rules. It was also chemically analyzed to determine the chemical composition.

In the present paper, we report our findings on the YB_{25} phase as a preliminary result of our investigations on one of the two new phases.

EXPERIMENTAL

In the earlier stage of experiments polycrystalline samples of nominal composition [B]/[Y] = n were prepared by the borothermal reduction method as follows:

$$Y_2O_3 + (2n + 3)B \rightarrow 2YB_n + 3BO.$$

Y_2O_3 powder (4 *N*, Shin-Etsu Chemical Co., Japan) and amorphous B powder (3 *N*, Callery Inc., USA) were thoroughly mixed and isostatically pressed into a pellet at 300 MPa. Later, Y_2O_3 powder was replaced with YB_4 powder (3 *N*, Nihon Shinkinzoku Co., Japan) for easier handling. The samples were heated to a predetermined temperature of about 1700°C and maintained for 1 h in vacuum using an RF furnace. In order to avoid carbon contamination during the reaction, the reaction was performed in a BN crucible surrounded by an inductively heated carbon-free composite susceptor which consists of BN, AlN, and TiB_2 (Denka Co., EC-composite). The reaction process mentioned above was repeated twice to ensure uniform composition of the product.

Both yttrium and boron content were determined by an ICP (inductively coupled plasma atomic emission spectroscopy) analysis after the powder was dissolved into conc. HNO_3 + conc. HCl (1 : 1) solution by keeping it at 110°C for about 12 h. Oxygen impurity was analyzed by a standard inert gas fusion method (Leco Co., TC-136). Carbon impurity was analyzed by a volumetric combustion method using a carbon determinator (Leco Co., WR-12).

Phase identification and determination of unit cell dimensions were carried out using a high resolution powder X ray diffractometer (Rigaku Co., RINT-1500) with Cu$K\alpha$ radiation. The peak intensities for the $K\alpha_1$ were determined after rejecting the $K\alpha_2$ peaks, using RINT software (Rigaku Co.). Unit cell dimensions were refined with a least-squares program, UNITCELL (6).

The electron diffraction patterns were derived at an acceleration voltage of 100 kV using a standard transmission electron microscope (Hitachi H-500).

RESULTS AND DISCUSSION

During phase analysis work on YB_{50}, it was already known that a less boron-rich phase exists between

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TABLE 1
YB_{25} X Ray Powder Diffraction Data

h	*k*	*l*	d_{calc} (nm)	d_{obs} (nm)	I/I_1	*h*	*k*	*l*	d_{calc} (nm)	d_{obs} (nm)	I/I_1
1	1	0	0.64602	0.64630	57	−2	1	3	0.17458	0.17459	10
0	2	0	0.51601	0.51601	15	2	1	3	0.17356	0.17357	6
0	1	−1	0.50938	0.50895	8	0	6	0	0.17200	0.17203	13
−1	0	1	0.48000	0.48023	5	−4	3	1	0.17012	0.17008	5
1	0	1	0.47648	0.47639	5	4	0	−2	0.16971	0.16973	10
−1	2	1	0.35145	0.35133	53	4	0	2	0.16847	0.16852	6
1	2	1	0.35007	0.35010	56	−1	5	2	0.16546	0.16541	6
2	1	−1	0.32243	0.32247	37	1	5	2	0.16517	0.16516	7
2	1	1	0.32031	0.32008	16	5	1	0	0.16358	0.16354	11
1	3	0	0.31770	0.31773	33	1	6	−1	0.16192	0.16195	4
0	3	1	0.29663	0.29635	5	1	6	1	0.16179	0.16172	5
0	0	2	0.29284	0.29294	27	4	4	0	0.16150	0.16148	6
−1	1	2	0.26733	0.26735	9	4	2	−2	0.16122	0.16125	5
1	1	2	0.26611	0.26597	11	3	0	−3	0.16000	0.16002	7
0	4	0	0.25801	0.25794	4	−5	0	1	0.15975	0.15971	4
0	2	−2	0.25469	0.25475	100	3	0	3	0.15883	0.15881	9
−3	0	1	0.25052	0.25041	7	2	3	−3	0.15748	0.15747	3
3	0	1	0.24902	0.24900	12	−1	4	3	0.15318	0.15320	4
−2	3	1	0.24161	0.24162	40	3	2	−3	0.15283	0.15286	4
2	3	1	0.24071	0.24069	27	3	2	3	0.15180	0.15177	4
−2	0	2	0.24000	0.23994	7	5	3	0	0.14927	0.14932	3
2	0	2	0.23824	0.23811	8	0	0	4	0.14642	0.14640	6
1	4	1	0.22688	0.22701	14	3	5	−2	0.14425	0.14427	3
3	2	−1	0.22536	0.22538	49	0	5	3	0.14183	0.14187	3
3	2	1	0.22427	0.22425	58	4	1	−3	0.14127	0.14124	5
2	4	0	0.21899	0.21908	18	0	2	4	0.14086	0.14090	4
−1	3	2	0.21565	0.21563	31	4	1	3	0.14020	0.14017	5
1	3	2	0.21500	0.21504	31	2	6	−2	0.13981	0.13984	5
4	0	0	0.20710	0.20701	10	2	6	2	0.13946	0.13945	6
1	5	0	0.20028	0.20036	23	6	0	0	0.13806	0.13809	4
3	1	−2	0.19794	0.19799	7	3	4	−3	0.13598	0.13593	3
3	1	2	0.19646	0.19641	4	3	4	3	0.13525	0.13526	14
0	5	1	0.19467	0.19474	3	2	5	−3	0.13442	0.13445	11
0	4	2	0.19359	0.19356	6	2	5	3	0.13395	0.13394	7
4	1	−1	0.19230	0.19229	17	−5	3	2	0.13337	0.13335	12
4	1	1	0.19140	0.19137	11	2	2	4	0.13306	0.13305	6
−1	0	3	0.19035	0.19046	4	1	3	4	0.13283	0.13286	8
1	0	3	0.18969	0.18968	4	5	3	2	0.13261	0.13261	10
−3	4	1	0.17973	0.17978	11	4	6	0	0.13232	0.13227	3
3	4	1	0.17917	0.17918	11	3	7	0	0.13006	0.13005	4
−2	5	1	0.17636	0.17638	15	5	5	0	0.12920	0.12922	13
2	5	1	0.17601	0.17600	13						

$[B]/[Y] = 20$ and 30. In order to establish a single phase composition of this unknown boride phase, powder syntheses with mixing ratios of $n = 20$, 25, 30, and 35 were carried out. It turned out that the single phase was not established. The powders of $n = 20$ and 25 were mixtures of YB_{12} and the unknown phase, while powders of $n = 30$ and 35 were mixtures of the unknown phase and YB_{50}. With increasing *n*, the diffraction intensity of $I_{unknown}$ reached a maximum at $n = 25$ and then a second maximum at $n = 30$. This indicates that the single phase of the unknown phase exists beyond but close to $n = 25$. More precise powder syntheses with different mixing ratios of $n = 24$, 24.5, 25, 25.5, 26, 26.5, and 27 were carried out. Single phases of the

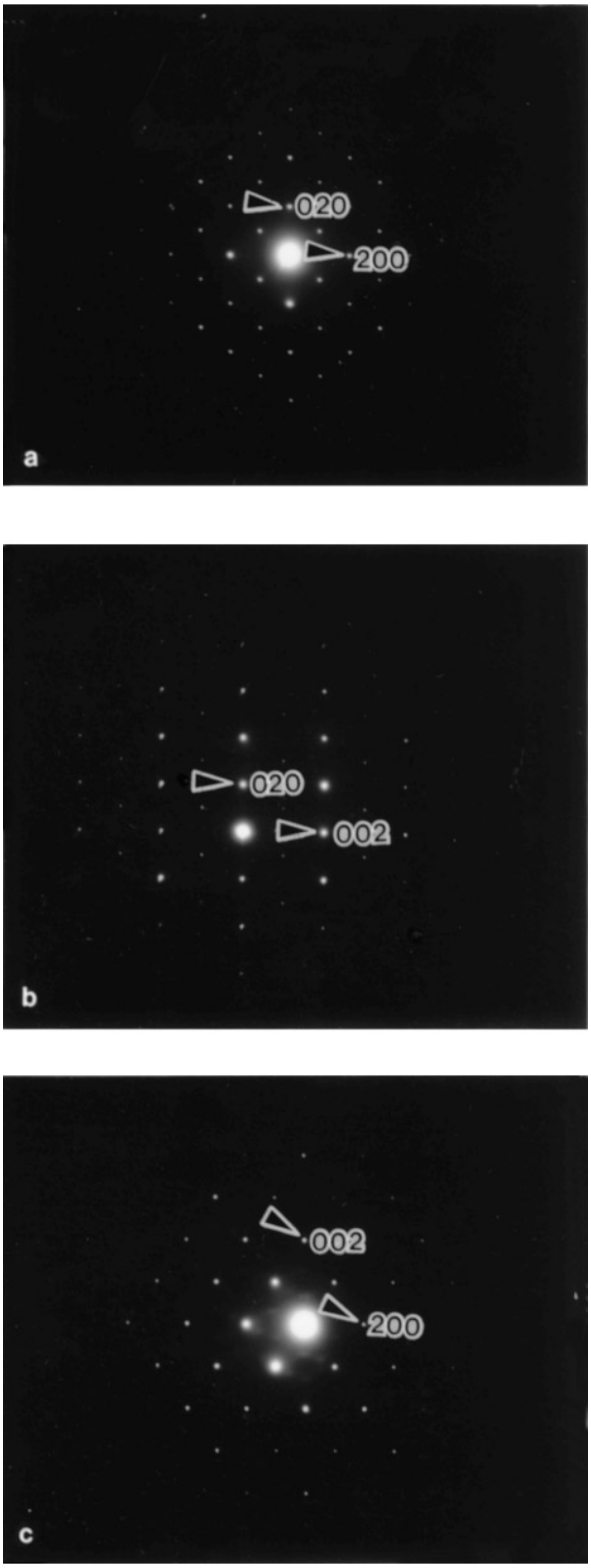

FIG. 1. Electron diffraction patterns of YB_{25} in (a) a^*–b^*, (b) b^*–c^*, and (c) c^*–a^* planes.

unknown phase, expressed as YB_{25}, appeared at mixing ratios of $n = 25.5$ and 26.0.

A powder sample for structure analysis was synthesized at $n = 25.8$ under the same reaction conditions mentioned above. Chemical analysis showed that the composition of the obtained powder was $[B]/[Y] = 24.8$. The difference between the mixing ratio and the chemical composition is due to ignition losses of raw powders of YB_4 and amorphous boron. The oxygen and carbon content of the powder obtained was about 0.3 wt% and 0.1 wt%, respectively.

X ray powder diffraction intensities for YB_{25} are presented in Table 1 together with the observed and calculated interplanar d-spacings, expressed as d_{obs} and d_{calc}, respectively. Electron diffraction patterns of the a^*–b^*, b^*–c^*, and c^*–a^* planes are shown in Figs. 1a, 1b, and 1c, respectively. The *hkl* assignments for both X ray diffraction peaks and electron diffraction spots were carried out according to a monoclinic body-centered cell with $a = 0.82842(3)$ nm, $b = 1.03203(3)$ nm, $c = 0.58570(2)$ nm, and $\beta = 90.402(3)^\circ$. Extinction rules obtained from both the electron diffraction patterns and the full indexing of the X ray diffraction peaks indicated that the structure belongs to one of the space groups $I121$(No. 5), $I1m1$(No. 8), and $I12/m1$ (No. 12) (7).

It is of interest to compare YB_{25} with $YAlB_{14}$, which is isostructural to $MgAlB_{14}$. $MgAlB_{14}$ has a body-centered orthorhombic structure (8). Data from both crystals are compared in Table 2. Unit cell dimensions of $YAlB_{14}$ are close to those of YB_{25}. In $YAlB_{14}$, both Y and Al atomic positions have partial occupancies of about 0.6–0.7 (9). Therefore the real $[B]/[Y]$ ratio in the $YAlB_{14}$ structure is nearly 25. It is reasonable to speculate that the crystal structure of YB_{25} is close to that of $YAlB_{14}$. The Al sites have become vacant or Y atoms redistribute into both the Al and the Y sites in the latter structure. The decrease in valence electrons caused by the lack of Al may distort the orthorhombic $YAlB_{14}$ structure into the monoclinic YB_{25} structure with $\beta = 90.4^\circ$. Rietveld analysis and/or single crystal diffraction analysis are necessary to understand more precisely the crystal structure of YB_{25}.

The YB_{25} phase is stable up to 1850°C. Above this temperature it decomposes into YB_{12} and YB_{66} without melting. This makes it difficult to grow a single crystal of YB_{25} by the melt growth method. It may be possible to obtain a sizeable grain for X ray single crystal diffraction analysis by a high temperature solution growth method using metal fluxes such as Al, Ga, Sn, and Sb and/or a grain growth method. Al flux, which is often used for high temperature solution growth of higher borides, is not usable for the present YB_{25} growth because $YAlB_{14}$ crystals will grow from the flux. Ga, Sn, and Sb fluxes were also unsuccessful for that purpose. Hot-pressing should be done not only for grain growth but also to obtain a bulky sample for physical property measurements.

TABLE 2
YB_{25} and $YAlB_{14}$ Crystal Data

Formula unit	YB_{25}	$YAlB_{14}$ [9]
Crystal system	Monoclinic	Orthorhombic
a (nm)	0.82842(3)	0.81947(6)
b (nm)	1.03203(3)	1.04130(8)
c (nm)	0.58570(2)	0.58212(3)
β (°)	90.402(3)	
V (nm^3)	0.50073(3)	0.4967
Space group	$I121$, $I1m1$, $I12/m1$	*Imam*

It would be very interesting to find out whether other rare earth elements can form phases isostructural to YB_{25}. Reaction experiments for Sc and from La to Lu showed that Gd to Ho can form phases of YB_{25} structure-type. Lattice constant measurements of those phases are underway.

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