JOURNAL OF MATERIALS SCIENCE 33 (1998) 4141–4145

Morphology and microstructure investigations of YB_{66} nano-particles prepared by plasma chemical process

J. Y. HUANG*, T. ISHIGAKI, T. TANAKA, S. HORIUCHI
National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan
E-mail: horiuchi@nirim.go.jp

Nanocrystalline particles of YB_{66} were prepared by plasma chemical process, using starting powders of YB_4 and B, and the morphology was examined by high-resolution transmission electron microscopy (HRTEM). The average grain size of the YB_{66} particles is less than 100 nm. All the YB_{66} nano-particles are cubic in shape, suggesting that they have been formed through a direct coagulation from a vapor phase. Facetting at the cube corners occurs in most particles. The [0 0 1] and [0 1 1] lattice images of a cubic particle with edge-length of 84 nm were obtained. The simulated and experimental images match very well. A considerable amount of coarse, nearly spherical YB_6 particles and unreached boron were additionally found by HRTEM. © *1998 Kluwer Academic Publishers*

1. Introduction

YB_{66} has recently received much attention in some contexts. Because of its large interplanar distance ($d = 0.586$ nm for the (4 0 0) reflection) and the absence of intrinsic absorption, it has been recently selected as a unique candidate for a soft X-ray monochromator in the 1–2 KeV region for synchronton radiation [1]. The basic unit in YB_{66} structure is the so-called supericosahedra consisting of $13B_{12}$ icosahedra [2]. These B_{156} units are composed of a central B_{12} icosahedron with $12B_{12}$ icosahedra bonded to each of the 12 vertices of the central B_{12} unit. This kind of structure is closely related to the recent topics such as quasicrystal and fullerene [3, 4]. Some quasicrystals are composed of icosahedron units and have icosahedral symmetry. The prototypical fullerene C_{60} has also an icosahedral symmetry and, therefore, how the icosahedral units can be linked in YB_{66} is highly relevant to understanding the structure of fullerene materials.

The reported preparation methods of YB_{66} powder included the direct melting of yttrium and boron [5] or the solid-state reaction between YB_4 and boron [1]. In the present paper, an alternative method, i.e. the thermal plasma chemical method, was employed to prepare nanocrystalline YB_{66} (n-YB_{66}) particles. The thermal plasma has a very high temperature, above 10 000 K, and the materials injected into the plasma are heated to melt and evaporate in 10–20 ms. In the downstream, the plasma is cooled very rapidly at the rate of 10^{6-7} K s^{-1}. The rapid quenching gives rise to the supersaturation in a vapour phase and the high density of nucleation. Fine particles are formed mostly through the coagulation from a vapour phase. A purpose of the present work is to examine the geometry of the particles in the Y–B system by high-resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

The induction plasma torch used has been reported elsewhere [6]. The plasma was generated at frequency of 2 MHz and a plate power of 40 kW. Three gas streams, such as the powder carrier gas (Ar at a flow rate of 4 l min^{-1}), the plasma gas (Ar at 6 l min^{-1}) and the sheath gas (Ar and H_2 at 30 and 3 l min^{-1}, respectively), were introduced into the torch. The plasma is confined in a 46 mm i.d. water-cooled quartz tube. The plasma discharges into a water-cooled stainless steel chamber in which the absolute pressure was maintained at the 40 ± 1 kPa.

The starting materials, YB_4 (Japan New Metals Co. Ltd., particle size 3–4 μm, purity 3 N) and boron powders (SB-Boron Corp., particle size 50 nm, purity 3 N), were mixed in ethanol. The dried mixture was axially injected into the centre of the discharge through a powder-injection probe with carrier gas at the feed rate of ~ 7 g min^{-1}. The plasma-treated powders were collected on the quartz wall of a 150 mm i.d. tube set below the plasma torch.

The crystalline phase in the plasma-treated powder was identified by X-ray diffraction (XRD) using CuK_α

*On leave from Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Chinese Academy of Science, Shenyang 110015, People's Republic of China.

radiation. The powders grown from a vapour phase, which consisted of very fine particles, were mounted on carbon-coated micro-grids and observed by high-voltage HRTEM (Hitachi, model H-1500) operated at 800 kV.

3. Results and discussion

3.1. Morphology

Fig. 1 is the XRD pattern of the obtained powders. The main diffraction peaks can be indexed by YB_{66}, YB_6, YB_{12} and YB_4. YB_{66} is the strongest in intensity and, therefore, is the main resultant phase.

Fig. 2 shows a general morphology of the powders. It is seen that the particles with different morphology and various size exist. Most particles seem cubic or rectangular and the average grain size is less than 100 nm.

The structure of the particles was characterized by HRTEM. Fig. 3a is the TEM image of a relatively coarse cubic grain. The grain size is about 350 nm; its corresponding electron diffraction pattern (EDP) in Fig. 3b) shows the exact [0 0 1] orientation. Facetting along (1 1 0), (1 2 0), etc., is observed at the corners. Interference patterns arise at the inner part of the grain. This may result from the overlapping of two grains with the same orientation but slightly rotated to each other; according to the simulation of the interference the rotation angle must be about 2°. The cube can be vacant at the core. In this case the two grains correspond to the walls at the top and bottom sides.

Coarse spherical particles were sometimes found. Their size ranges from 5 to 10 μm. Habit planes are locally visible, suggesting that the particle is not spherical but strictly polyhedral. An image of a typical particle and its corresponding EDP are shown in Fig. 4(a) and (b), respectively. EDPs can be identified by YB_6. The contrast is much darker in the YB_6 than that of YB_{66} mentioned above. This is because the specific gravity of the former is higher than that of the latter.

Ultra-fine particles of about 10 nm were locally observed, as shown in Fig. 5(a). Reflections in the corresponding EDP of Fig. 5(b) are diffuse, as was the

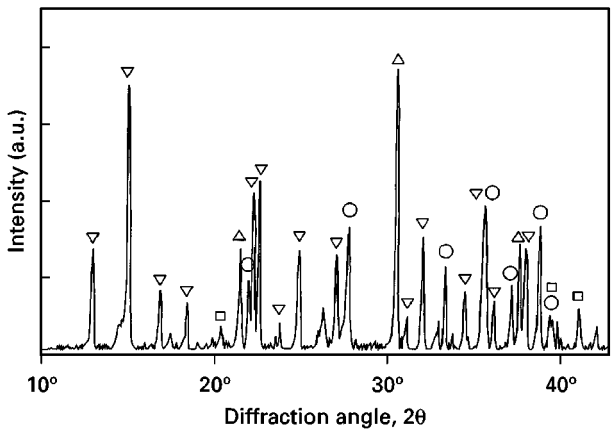

Figure 1 XRD pattern of yttrium borides prepared by the plasma chemical process. CuK_α radiation is used. The main phase is identified to be YB_{66} ▽, YB_{66}; △, YB_6; ○, YB_4; □, YB_{12}.

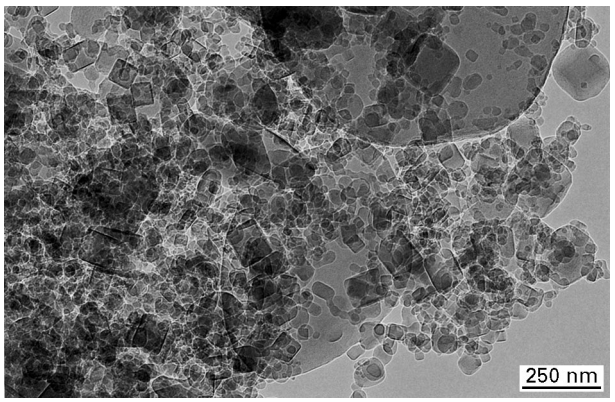

Figure 2 TEM micrograph showing the morphology of yttrium boride powders. Most particles are cubic and each particle consists of a single grain.

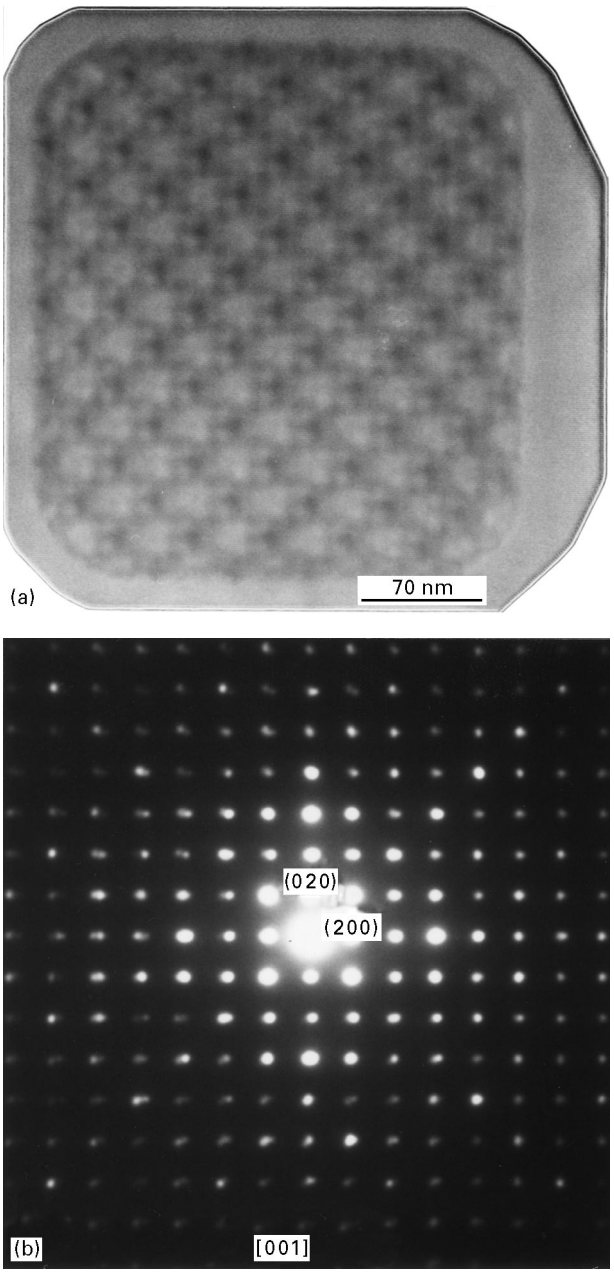

Figure 3 (a) TEM micrograph of a cubic YB_{66} grain in the [0 0 1] orientation; facetting at the corners can be observed. Interference pattern is visible in the centre part of the grain. The interior of the grain is probably empty. (b) EDP corresponding to the grain in (a).

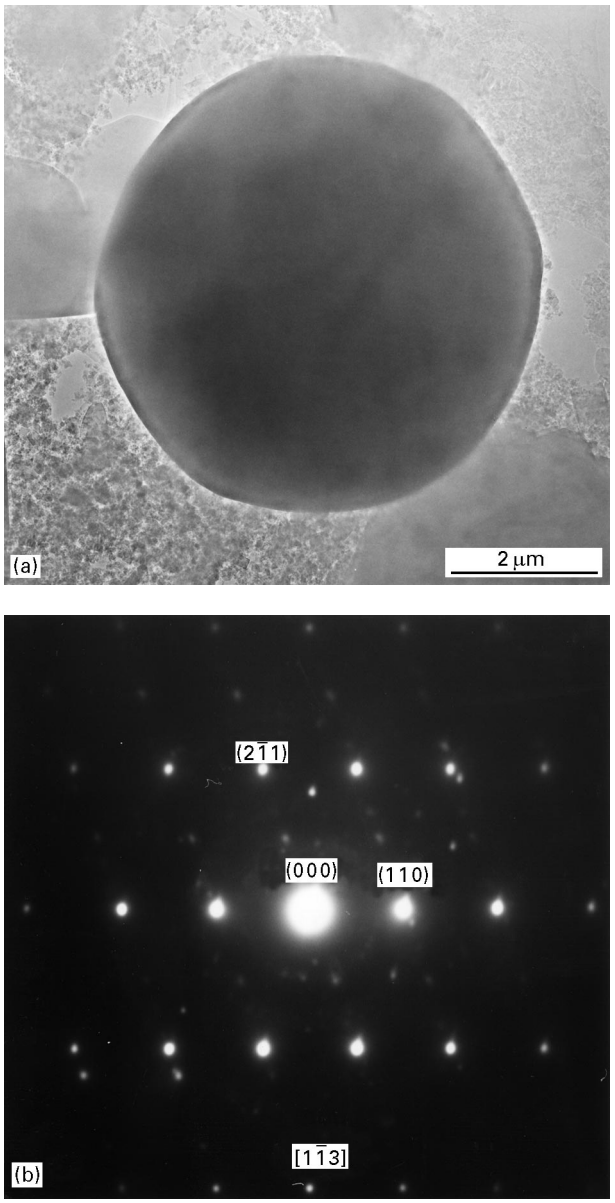

Figure 4 (a) Morphology of a spherical YB_6 grain. Weak habit planes are visible. (b) EDP of the particle in (a).

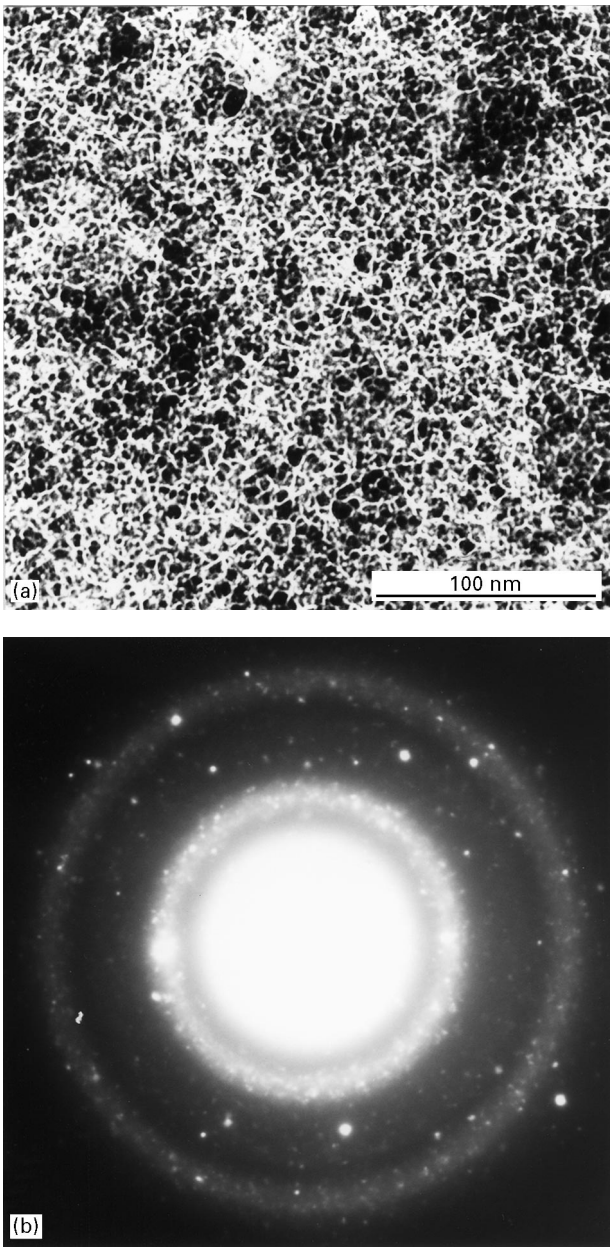

Figure 5 (a) Morphology of the unreacted boron. (b) EDP corresponding to (a). Spotty reflections may be from YB_{66}.

case for those from the starting boron, showing that they are amorphous. It is thus concluded that much unreacted boron remained in the end products. The reason for the missing diffraction peaks of boron in the XRD pattern of Fig. 1 may be as follows. Firstly, the scattering factor of boron is about $\frac{1}{5}$ lower than that of yttrium and its diffraction intensity is thus 25 times lower. Secondly, the boron is amorphous so that its intensity is strongly reduced.

YB_4 particles do not show any particular morphology, although they are detected as a minor component in the XRD chart of Fig. 1. They are probably from the starting materials. For YB_{12}, which is included slightly in Fig. 1, we have not found the EDP.

The mechanism for the morphology formation has been subject of much discussion. Suzuki *et al.* proposed that the particle morphology depends on its crystal structure. They synthesized many kinds of oxide fine powders by spray pyrolysis of aqueous salt solutions in r.f. induction plasma [7]. From the observation of the powders they concluded that at an early stage of crystal growth from the gas phase the particle morphology reflects the crystal structure. The powders had a diameter range between 15 and 35 nm and the shape of the oxides with monoclinic, cubic and tetragonal structures was spherical, while that with hexagonal was laminar. On the other hand, Ishigaki *et al.* suggested that the particle morphology is determined by the supersaturation condition. Cubic nano-particles of titanium carbide were synthesized by coagulation from a vapour phase in a thermal plasma [8]. They were concluded to be formed under the low degree of supersaturation of the vapour during cooling. Besides, alumina particles coagulated from the vapour showed various morphology also depending on the degree of supersaturation [9]. When the supersaturation was considerably high, the nucleation and subsequent coalescene occurred as the liquid phase and the products were spherical. In contrast, under the relatively low supersaturation, the coagulation

occurred directly from a vapour phase. In the present work the raw mixture injected into a thermal plasma has partially melted and evaporated. The fine cubic YB_{66} particles must have been coagulated directly from the vapour. On the other hand, the coarse spherical YB_6 particles must have been formed through the reaction between the melted YB_4 and boron. This is supported by the fact that unreacted YB_4 and B were detected after the plasma treatment.

3.2. Microstructure of YB_{66}

The structure of YB_{66} is based on a fcc lattice ($a = 2.345$ nm) with a unit cell that contains approximately 1600 boron atoms, of which 1248 are assigned to eight B_{156} units. The remaining boron atoms have been assigned to non-icosahedral structures consisting of B_{48} units or a mixture B_{48} and B_{36} units [2]. More recent work assigns the non-icosahedral boron to a B_{80} unit in which 50% of the sites are occupied [10]. All the yttrium atoms randomly occupy approximately 50% of the metal atom sites, giving about 24 yttrium atoms per unit cell. Besides, scanning tunnelling microscopy images of YB_{66} [0 0 1] revealed that B_{156} supericosahedra indeed exist as discrete structural entities [11].

In the present experiment, both [0 0 1] and [0 1 1] lattice images of a cubic nano-particle with edge-length of 84 nm were obtained from the identical particle (Figs 6a and 7a). Because the tilting angle in our microscope is from -25° to 25°, it can happen that the [0 0 1] and [0 1 1] orientations locate at the opposite tilting directions. It is seen in Fig. 6(a) and Fig. 7(a) that the surface of the particle is not flat but contains many steps. No amorphous layer is detected at the surface. Even in this small particle the facetting at the corner is visible. Based on Richards and Kasper's structural model, the [0 0 1] lattice image was simulated using the Mac–Tempas program. Fig. 8(a) is the simulated images, changing the thickness and defocus, while Fig. 8(b) is the experimental one magnified from a part of Fig. 6(a). The accelerating

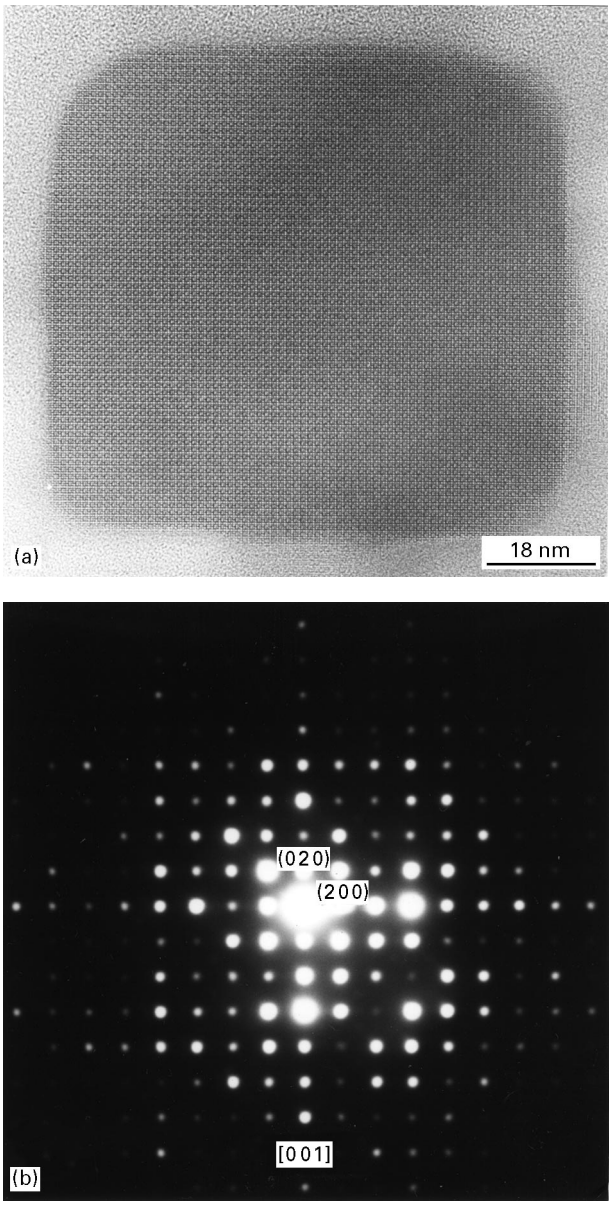

Figure 6 (a) HRTEM image of a cubic YB_{66} nanocrystal in the [0 0 1] orientation; (b) EDP corresponding to (a).

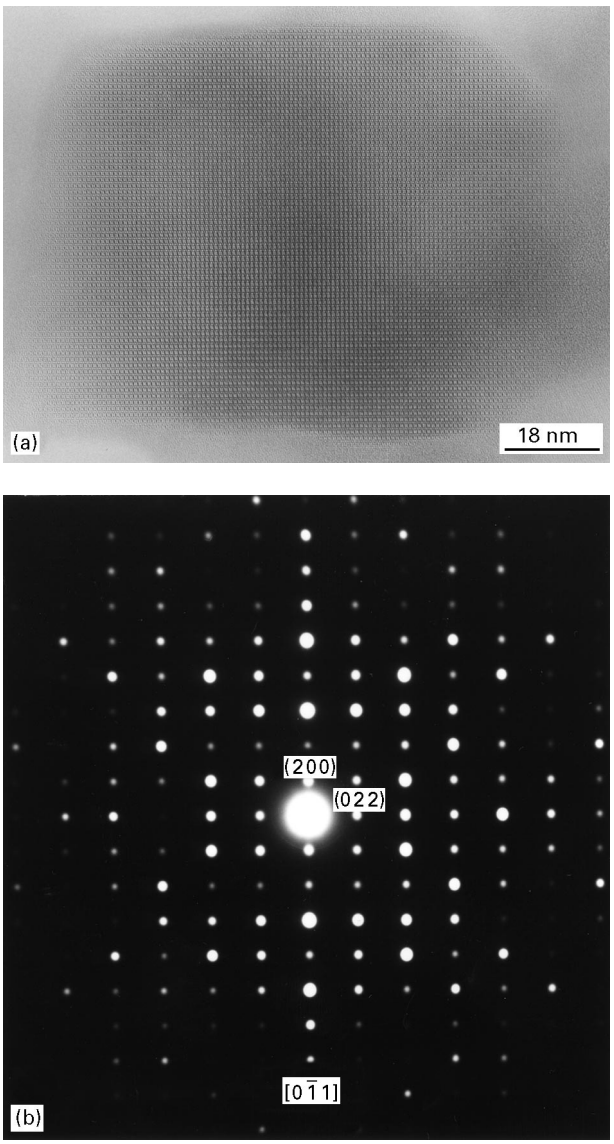

Figure 7 (a) HRTEM image of the same grain as shown in Fig. 6(a) but in the [0 1 1] orientation; (b) EDP corresponding to (a).

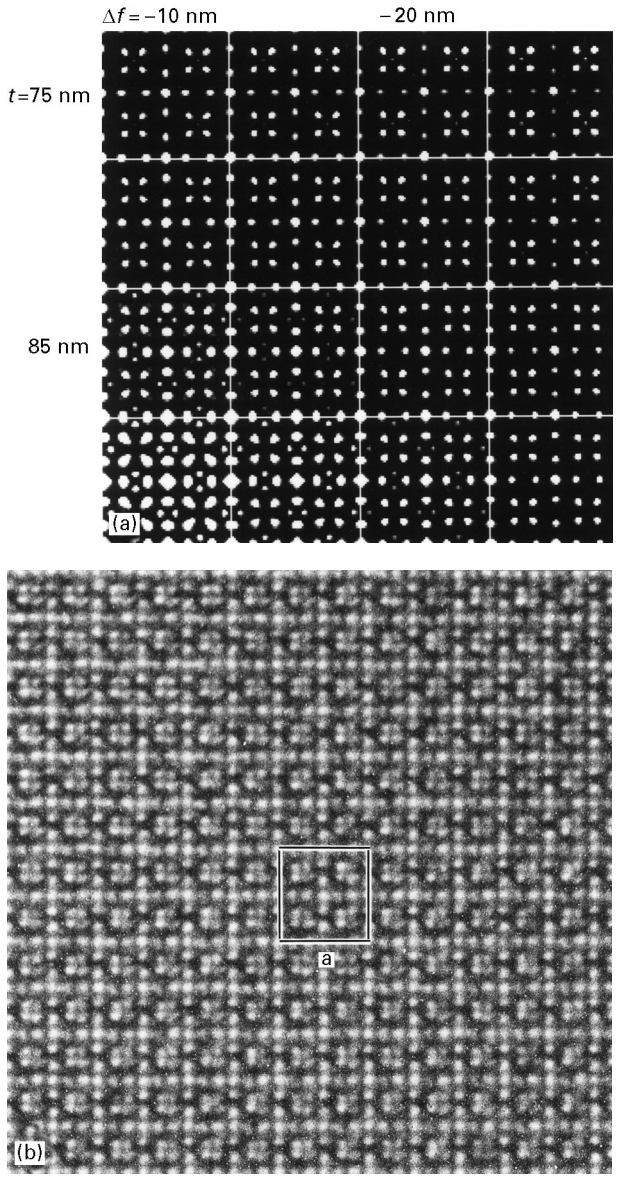

Figure 8 (a) Simulated images of YB_{66} [0 0 1]; t: thickness, Δf: underfocus amount. (b) Experimental image enlarged from Fig. 6(a) showing that the best match between the experimental image and the simulated one appears at the thickness of about 80 nm which is equal to the edge length of the cubic grain. $a = 2.345$ nm.

voltage was taken as 800 kV, the spherical aberration constant 2.2 mm, the focus spread was caused by chromatic aberration of 10 nm and the convergent beam angle was 0.8 mrad. It is seen that the calculated and real images match very well at the underfocus of about 20 nm. The bright spots correspond to the channels among the column of supericosahedra. Because the shape of the particle is cubic, the thickness of the specimen should be equal to the edge length of the cube, i.e. 84 nm. This is in agreement with that the best match to the experimental image occurring at the specimen thickness of around 80 nm.

4. Conclusions

The normal preparation methods of YB_{66} include the direct melting of yttrium and boron or the floating zone technique. In the present paper we used an alternative method, i.e. the plasma chemical method. The XRD of the product has indicated that the phases are mainly YB_{66} with minor component of YB_6 together with a small amount of YB_4 and YB_{12}. TEM observations showed that unreacted amorphous boron still exists. There are two typical morphologies; one is a cube with size from a few to a few hundred nm and another a sphere from 5 to 10 &Lm, which correspond to YB_{66} and YB_6, respectively. The interior of some large cubes (about 350 nm) are probably empty. HRTEM images of a fine YB_{66} particle shows that there are no defects. The computer-simulated image matches with the experimental one, which suggests that the structural model of YB_{66} proposed by Kasper et al is reasonable.

References

1. T. TANAKA, Y. ISHIZAWA, J. WONG, Z. U. REK and M. ROWEN, *Jpn. J. Appl. Phys. Series* **10** (1994) 110.
2. S. M. RICHARDS and J. S. KASPER, *Acta Crystallogr.* **B25** (1969) 237.
3. C. JANOT, "Quasicrystals – a primer" (Clarendon Press, Oxford, 1992).
4. P. A. HEINEY, in "The fullerrenes", edited by H. W. Kroto, J. E. Fischer and D. E. Cox (Pergmon Press, New York, 1993) p. 163.
5. A. U. SEYBOLT, *Trans. Amer. Soc. Met.* **52** (1960) 971.
6. T. ISHIGAKI, Y. MORIYOSHI, T. WATANABLE and A. KANZAWA, *J. Mater. Res.* **11** (1996) 2811.
7. M. SUZUKI, M. KAGAWA, Y. SYONO and T. HIRAI, *Ceram. Trans.* **22** (Ceramic Powder Science IV) (1991) 147.
8. T. ISHIGAKI, J. JUREWICZ, J. TANAKA, Y. MORIYOSHI and M. I. BOULOS, *J. Mater. Sci* **30** (1995) 883.
9. T. ISHIGAKI, Y. BANDO, Y. MORIYOSHI and M. I. BOULOS, *ibid.* **28** (1993) 4223.
10. I. HIGASHI, K. KOBAYASHI, T. TANAKA and Y. ISHIZAWA, *J. Solid State Chem.* **133** (1997) 16.
11. C. L. PERKINS, M. TRENARY and T. TANAKA, *Phys. Rev. Lett.* **77** (1996) 4772.

Received 12 August 1997
and accepted 11 May 1998