Floating-zone crystal growth of Nb-doped YB_{66} for soft X-ray monochromator use

T. Tanaka[a]*, **A. Sato**[b], **S. Takenouchi**[b], **K. Kamiya**[c], **T. Numazawa**[c]

[a] Advanced Materials Laboratory, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
[b] Technical Support Section, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
[c] High Magnetic Field Center, National Institute for Materials Science, Sakura 3-13, Tsukuba, Ibaraki 305-0003, Japan

E-mail: `tanaka.takaho@nims.go.jp`

Abstract. Nb-doped YB_{66} single crystals were grown by the floating-zone method using a 4 ellipsoidal mirror-type xenon lamp image furnace. Nb-doping is expected to improve the performance of YB_{66} soft X-ray monochromators. Maximum site occupancy of Nb achieved was 95%. Full-width at half-maximum of the rocking curve measured for CuKα 10 0 0 reflection achieved 40-50 arcsec. Thermal conductivity of the crystal with the maximum site occupancy increased about two times that of undoped YB_{66} crystals.

Keywords: doping; floating-zone technique; borides; soft X-ray monochromator materials

1. Introduction

The YB_{66} soft X-ray monochromator is useful for dispersing synchrotron radiation in the energy range 1-2 keV and has been now in practical use after the first installation on BL3-3 at Stanford Synchrotron Radiation Laboratory [1]. National Institute for Materials Science (NIMS) beam line at SPring-8 successfully installed a YB_{66} double crystal monochromator in 2002 [2], however, flux density stayed at around an order of 10^9 counts/s, although the incident beam could be increased to a level of more than 10^{12} counts/s. The main reason for this is due to amorphous-like low thermal conductivity of about 2.3×10^2 W/cm/K at room temperature as well as low X-ray reflectivity of about 3%. The low thermal conductivity does not allow loading high flux density that would cause a thermal bump of the YB_{66} monochromator crystal and its high resolution would be lost.

YB_{66} has a face-centered cubic structure (space group: $Fm3c$ (No. 226)) with lattice constant of 23.4 Å [3]. Transition metal doping experiments on YB_{66} indicated that 5th and 6th group transition metals of V, Cr, Nb and Mo enter a special site of (1/4,1/4,1/4) in the unit cell. Structure factor calculation indicated that the occupation of this special site can increase the intensity of the 4 0 0 reflection, which is used for dispersing synchrotron radiation soft X-ray, by a factor of about 2 for Nb and Mo. Moreover, a special boron site of (0.235, 0.235, 0.235), which is expected to be a cause for amorphous-like low thermal conductivity by acting as a phonon scattering center, can be removed by the occupation of the special site. Thus we can expect improved performance of YB_{66} soft X-ray monochromator based on both, increases of X-ray reflectivity and thermal conductivity induced by the transition metal doping.

For monochromator application the crystals quality must be high, although the transition metal doping makes the crystal growth much more difficult than in the case of undoped YB_{66}. Rocking curve full-width at half-maximum (FWHM) values for CuKα 10 0 0 reflection of undoped YB_{66} ranged from 30 to 50 arcsec [4]. Transition metal-doped YB_{66} must achieve the same level of FWHM value. From several crystal growth experiments it was judged that a Nb-doped YB_{66} crystal could achieve a higher crystal quality than an Mo-doped one. Here we report the floating-zone crystal growth of Nb-doped YB_{66} crystal.

2. Experimental procedure

Before preparing feed rods for floating-zone crystal growth, raw powders with a desired composition were synthesized by reacting YB_4, NbB_2 (Japan New Metals Co Ltd., Japan) and amorphous B (SB-Boron Corp., USA) powders. After mixing these powders and compacting to a green rod by CIP (Cold Isostatic Press) process, the compacted rod was reacted under a carbon free crucible system at about 1700 °C for 10 h in vacuum using an RF heating furnace. The carbon free crucible system consisted of a BN crucible, a composite (TiB_2+BN+AlN) susceptor (Denka BN composite EC, Japan) and BN thermal insulation components. The obtained rod was so porous that it was pulverized once and then the powder was compacted again into a green rod. The compacted rod was sintered at about 1800 °C using the same system as this during reaction.

Floating-zone crystal growth was carried out using a 4 ellipsoidal mirror-type xenon lamp image furnace (Crystal Systems Inc., Japan). Both the feed rod and the growing crystal were driven downwards at 7 $\sim$ 10 mm/h and were counter rotated at 6 $\sim$ 20 rpm. Growth orientation was adjusted to the [0 0 1] or [0 1 1] direction. Atmosphere was flowing Ar gas.

The molten zone composition was always different from that of the growing crystal so that at the initial stage of the floating-zone crystal growth a suitable amount of pellet having a desired molten zone composition was set on a seed crystal. The zone passage started after forming the initial molten zone by melting the pellet.

The chemical composition, density and lattice constant of several parts of the crystals were determined by wet chemical analysis, buoyancy method and powder X-ray diffraction, respectively. For the wet chemical analysis, inductively coupled plasma atomic emission spectroscopy was used. For measuring the mass density, a highpurity Si single crystal was used as a standard. A high-purity Si powder was used as an internal standard in X-ray powder diffraction.

Crystal quality was evaluated by the double crystal rocking curve mapping method using the 10 0 0 reflection of the surface. The beam size of the incident CuKα X-ray was adjusted to be 1×1 mm^2 [4]. In order to determine the Nb site occupancy single-crystal X-ray diffraction (XRD) data were corrected using a CCD area detector (Bruker SMART APEX, Germany) with graphite monochromated MoKα radiation. Single-crystal specimens for XRD data collection were obtained by cracking a part of the FZ-grown crystals. The average size of the crystals used for the XRD measurements was 2×10^{-2} mm^3.

Thermal conductivity measurements were made using a standard steady heat flow method. A rod sample with dimensions of 2.5×3×15 mm^3 was cut parallel to the [0 0 1] direction from the FZ-grown single crystal by a high-speed diamond saw. Temperature differences during the thermal conductivity measurements were kept within 2% of the sample temperature.

3. Results and discussion

In general, in floating-zone crystal growth of doped samples problems may arise from the composition difference between the growing crystal and the molten zone. The maximum content of Nb in YB_{66} was roughly one-third of Y which is only 0.5 at%. The reduction of growth temperature by Nb-doping is expected to be small compared with the growth temperature of undoped YB_{66}. The partition coefficient of Nb at the growth interface is roughly 0.3, i.e. the molten zone contains a three times larger amount of Nb than the growing crystal. The freezing temperature of the molten zone corresponds to the growth temperature at the phase boundaries. The apparent density of the sintered feed rod stayed at around 60% because of poor sintering behavior of strongly covalent YB_{66}. During the floating-zone passage the lower melting point zone with high Nb content can infiltrate into the porous feed rod. Such infiltration could be observed during the crystal growth of undoped YB_{66}, however, high crystal quality could be achieved by the double zone passage [4], where the first zone passage aimed to consolidate the sintered feed rod and the second zone passage aimed to achieve high quality. In the case of Nb-doped YB_{66}, the lower melting point material infiltrates deeper than the case of undoped YB_{66} and swells up increasingly above the molten zone. This makes it difficult to achieve high-quality and high-Nb content even by a double zone passage.

Different ways were tried and the most effective way was a heat zone passage using the floating zone furnace, where the temperature at the heat zone was kept just below the melting temperature. Such high temperature could make the feed rod nearly 100% dense by sintering. Zone pass rate was set at 400-500 mm/h and power density was

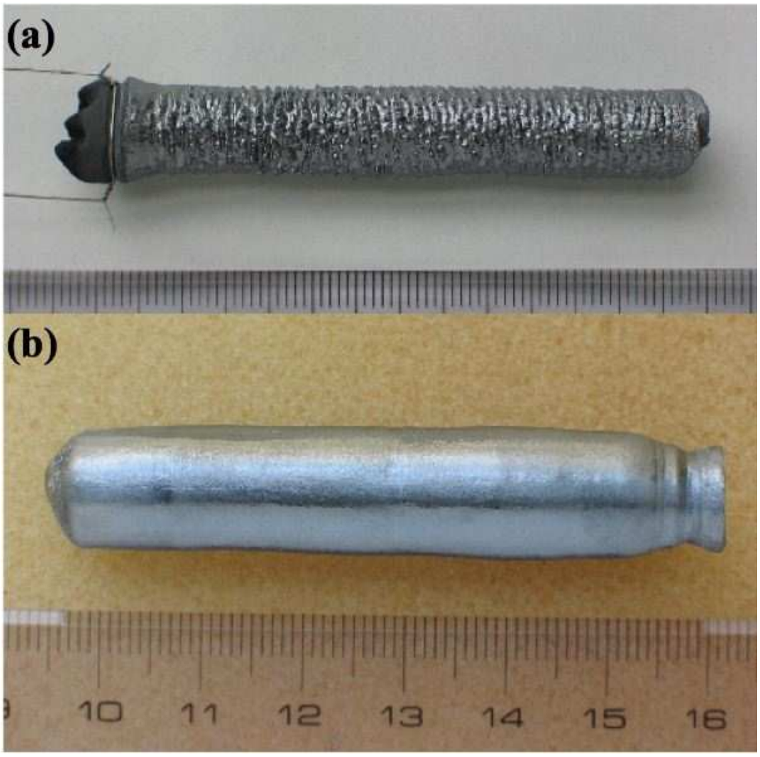

Figure 1. (a) A feed rod consolidated by two zone passages and (b) a grown single crystal of $YNb_{0.30}B_{62}$. A part of the frozen molten zone remained on the left side end of the crystal. Growth orientation was [0 1 1].

about 90% of that used for the molten zone passage. This combination of the high travel rate and the high power density allowed the feed rod sintering without forming the molten zone. An even higher translation rate could break the consolidated part of the rod by thermal shock and a lower power density could not consolidate the feed rod sufficiently. A rod passed twice by the heat zone is shown in Fig. 1(a). The thin surface layer melted during the second heat zone passage, which could maintain surface smoothness of the feed rod and could make the final floating-zone passage more stable.

Varying [B]/[Y] composition ratios were tried, for instance, the yttrium-richest composition of [B]/[Y]=58; a middle composition of [B]/[Y]= 62; which is the congruent composition for undoped YB_{66} [5], and a boron-rich composition of [B]/[Y]=66. Chemical compositions, densities and lattice constants of grown crystals with yttrium-rich composition are summarized in Table 1 as an example. The partition coefficient of Nb at the growth interface is roughly 0.3. The number of Nb atoms in the unit cell is 6, which agrees with the site occupancy of 75% determined by structure analysis. The chemical composition, density and lattice constant measurements of crystals indicated that the number of boron atoms in the unit cell is 1634 on an average and almost independent of the number of yttrium atoms in the unit cell. Since the maximum number of Nb in the unit cell is 8, Nb content was compared to B.

Table 1. Chemical compositions, densities and lattice constants of a grown crystal.

Position	Chem. Comp.	Density (g/cm^3)	a (Å)
Feed rod	$YNb_{0.24}B_{56.3}$		
Zone	$YNb_{0.63}B_{45.5}$		
Xtl z-end	$YNb_{0.22}B_{58.4}$		
Xtl middle	$YNb_{0.22}B_{57.8}$	2.6552	23.4763^a
Xtl initial	$YNb_{0.21}B_{58.6}$	2.6494	23.4855^a

An example of a grown crystal is shown in Fig. 1(b). Post-growth deposition on the surface of the grown crystal could happen. The crystal surface seemed dull because small crystallites deposited.

Slices with surfaces parallel to (1 0 0) were cut from the grown crystals. Next to the central part of the crystal a single-peak rocking curve with FWHM value of 48 arcsec could be observed as shown in Fig. 2. However, uniformity through the whole crystal could not be achieved yet, often double peak rocking curves and peak position shift were also observed especially at peripheral parts of the crystals. Thus, intensity comparison of the 4 0 0 reflections between undoped and Nb-doped samples has not been successful yet.

Thermal conductivity of both undoped and Nb-doped samples was measured from 150 to 4K as shown in Fig. 3, where thermal conductivity of β-boron [6] is also shown for comparison. The site occupancy of the Nb-doped sample was 95%. For the measured value of the undoped one agrees with the previous literature data [7]. Temperature dependence of the Nb-doped sample was still amorphous-like, but the value increased

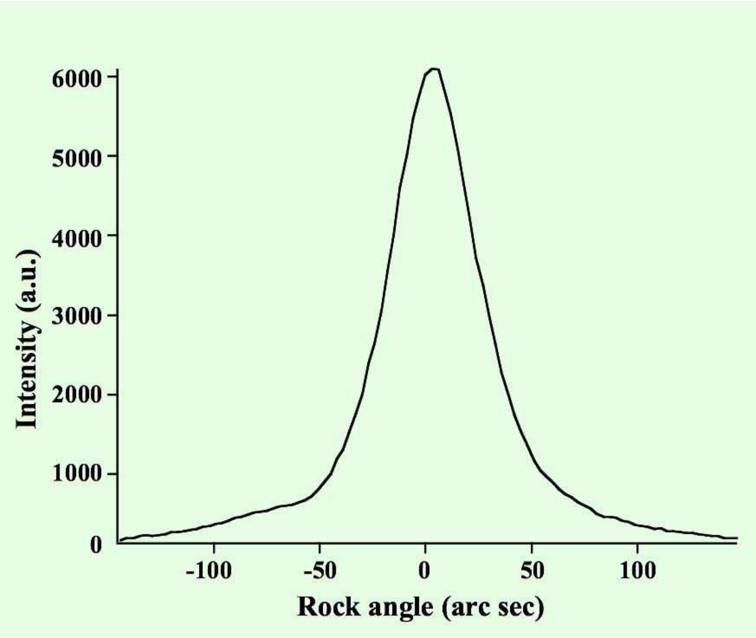

Figure 2. A rocking curve of CuKα 10 0 0 reflection measured in the central part of a grown single crystal of $YNb_{0.30}B_{62}$. FWHM is 48 arcsec.

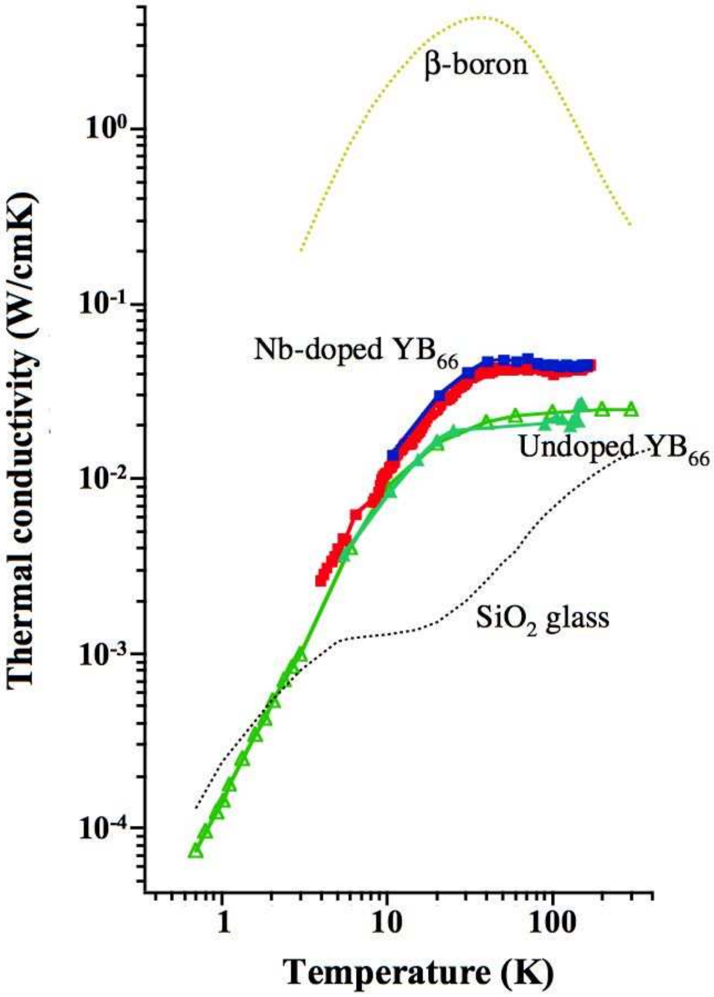

Figure 3. Thermal conductivity of a grown single crystal of $YNb_{0.32}B_{65.6}$ whose Nb site occupancy is 95% compared with that of undoped YB_{66} and β-boron. (solid rectangle-red and blue) Nb-doped YB_{66}, (open triangle-light green) literature data of undoped YB_{66} [7] and (solid triangl-light green) measured value of undoped YB_{66} and (dotted) literature data of β-boron [6].

by a factor of about 2 compared with that of the undoped sample. Five percentage of the 8 Nb sites are not occupied. Thus almost a half of unit cells can remain at least one special boron site, which acts as the phonon scattering center, without being replaced by the Nb occupation. The phonon mean free path of undoped YB_{66} calculated from the thermal conductivity coincides with its lattice constant. On the other hand, the phonon mean free path of the present crystal should be roughly 2 times the lattice constant. The expected increase in phonon mean free path agrees well with the thermal conductivity increase. We may expect an additional thermal conductivity increase by a further increase in the Nb site occupancy.

4. Concluding remarks

Highly Nb-doped YB_{66} single crystals could be grown by the floating-zone method. The obtained crystals showed partly a high quality comparable with undoped YB_{66}, but uniformity was not sufficient for practical application. Thermal conductivity of Nb-doped YB_{66} crystals is increased by a factor of 2 compared with that of the undoped one. The results give us a hope to achieve higher performance of the Nb-doped YB_{66} monochromators. Further improvement of the crystal growth process is underway.

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