Preparation of Isotopically Controlled β-B$_{105}$ Single Crystals by the Floating Zone Technique

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Abstract

Large single crystals of β-rhombohedral boron (β-B$_{105}$; space group: R$\bar{3}$m) ,whose isotopic composition was controlled, were prepared and the crystallographic uniformity and isotopic composition of the boron crystals were examined.

The crystal was grown by the floating zone refining method using a Xe lamp image furnace under Ar atmosphere. The growth rate was 10 mm /h and the flow rate of Ar gas was 10 ℓ /min . The sample was cut perpendicular to the growth direction. The orientation of crystal was measured by X-ray Laue technique. The microstructure was observed by optical microscope. Isotopic composition of the specimens was analyzed by grow discharge mass spectroscopy (GDMS).

The obtained isotopically modified crystal was 12 mm diameter and 45 mm length on the average. The ^{10}B enriched crystal was consisted of 93.21%^{10}B and 6.79%^{11}B. On the other hand, the ^{11}B enriched had 99.01%^{11}B and 0.99%^{10}B. By optical microscopic examination, grain boundaries were not observed in the large part of the cross section. According to X-ray Laue measurement, the growth direction of the crystal at any position of the cross section of the crystal rods was <10$\bar{1}$0>of the hexagonal crystalline system. This indicates that the isotopically modified β-boron crystal with high quality was obtained.

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Introduction

Many kinds of materials are composed of elements which consist of several stable isotopes. Isotope effect on lattice vibration properties such as lattice parameters, thermal conductivities, or, in some materials, on electrical conductivities has been observed for semiconductors. For example, the relative difference in the lattice constant of germanium single crystal between natural isotopic composition and the ^{74}Ge enriched crystals was investigated by theoretical and experimental approach [1].

Focusing on elementary boron, it is composed of only two stable isotopes, ^{10}B and ^{11}B with the abundance of 19.9% and 80.1%, respectively and is the material for easy isotope separation. The control of isotope composition of boron single crystal and the availability of isotopically modified crystals provide a new opportunity to investigate not only phonon properties but also electrical transport mechanism of boron rich solid which is influenced lattice vibration. Thus, we want to pay attention to the construction of elemental boron solids. The crystal structure of the boron solid has at least four modifications of the crystalline structure. A feature of these modifications is that the unit cell of boron or boron rich solid contains icosahedral structures based on B$_{12}$ clusters as subunits. This cluster is not isolated in nature. That is, atoms constituting inter- and intra-icosahedral structure are strongly bound by covalent bond based on so called three centered bonding. Therefore, the hardness of boron or boron rich solids is very high and the melting temperature is as high as over 2350K - a thousand degree greater than for silicon. Emin suggested the availability of novel application of the icosahedral boron rich solids such as $B_{12}P_2$, $B_{1-x}C_x$ because of their refractory properties [2]. Since relative mass difference between ^{10}B and ^{11}B is quite large, the large difference in zero point energy is expected. However, the measurement of lattice vibration properties has not been performed using the isotopically enriched boron single crystals so far. In order to study the isotopic effect on phonon related physical properties of boron crystals, we attempted to grow three different kinds of isotopically modified large boron (β-B$_{105}$ [3] ; space group R$\bar{3}$m) crystals by the zone melting technique.

Experimental

(a) The apparatus for crystal growth

As mentioned above, the melting point of elementary boron is 2365K. Floating zone technique not using a crucible is fairly suitable for the crystal growth of the refractory materials such as boron. The apparatus consists of an ellipsoidal reflector having a lamp as heat source positioned at one focus. At the other focus, the melting zone of the material was positioned. The heat source of the furnance was infrared ray emitted out from a Xe short arc lamp (6 kW).

(b) Preparation of the raw material rod

The raw material rods were prepared by a powder metallurgy method. Commercial powders of 99.5%^{10}B enriched, 99%^{11}B enriched and natural B were sealed in the rubber tubes of 10 mm in diameter .Then, the specimens were isostatically pressed to cylindrical shapes under hydrostatic pressure of 2000 kgW/cm^2. After this procedure, mold sample has still low density. Therefore, careful handling was required. Then, the above mold specimens were sintered in MgO or BN crucibles at 1600K for two hours under the vacuum of 75 mPa. The sintered rods obtained were 9 mm in diameter and 70 mm long. The color of the sintered rods was charcoal gray.

(c) Crystal growth

The raw material rod was suspended to the upper shaft and the seed crystal was fixed to the lower one. The seed crystal was at first grown by FZ method using natural boron polycrystal as raw materials. The crystalline orientation of the seed crystal was found to be <10$\bar{1}$0> by X-ray Laue method. So that, (10$\bar{1}$0) plane put into contact with the lower tip of the charge rod. Next, an atmosphere of pure argon was introduced into the quartz tube. The flow rate was as fairly large as 10 ℓ /min in order to avoid the problem that the boron vapors from the charge rod react with the transparent quartz tube. The shaft of the raw material rod and that of the seed crystal were slowly driven downward. The two shafts were counter-rotated at 15 rpm. The heat power was constantly supplied to keep the melting zone stable.

(d) Microstructual Analysis

The obtained crystal rod was cut perpendicular to the growth direction. and then polished metallurgically to mirror surface. Since the Mohs hardness of the boron solid is as large as 9.3, about one hour was required to cut the specimen by a diamond blade (ISOMET 2000 BUHLER). Polished cross sections were examined by a optical microscopy. The check of the growth direction of the crystal rod was performed by X-ray Laue back diffraction technique (30 mA×30 kV at a 30 mm stand-off distance). The isotopic composition of the crystals was analyzed by grow discharge mass spectroscopy (GDMS). Both Laue diffraction and GDMS measurements were made for several sheets cut from the rods and there was no clear

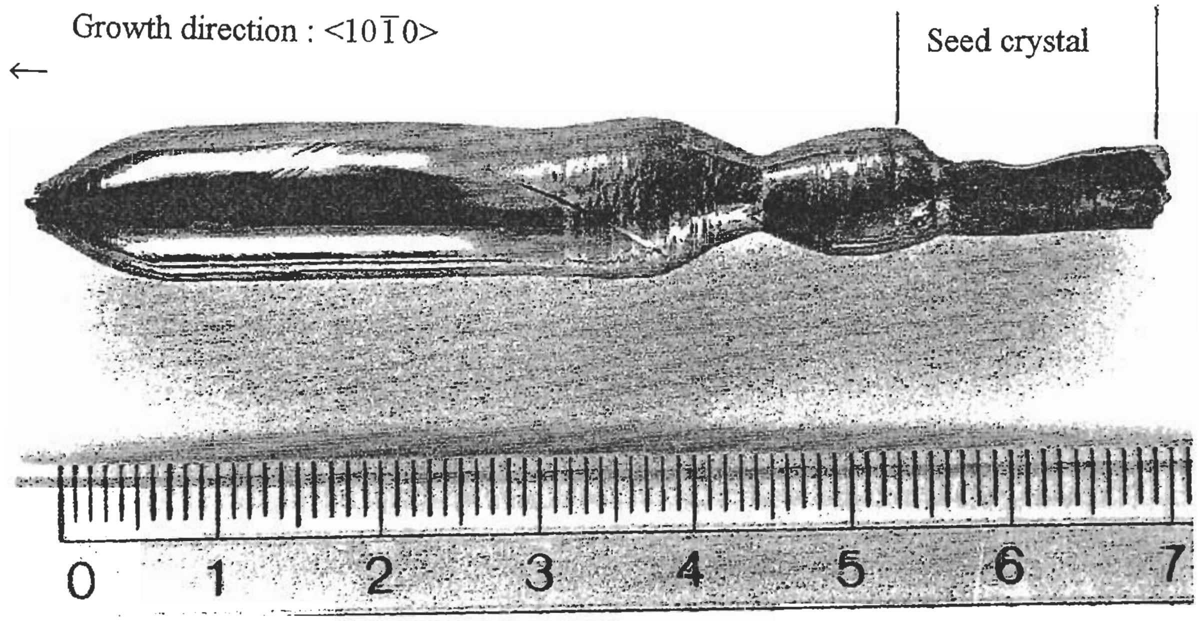

Fig.1 ^{10}B enriched β-B$_{105}$ crystal rod grown by the floating zone method using a Xe lamp image furnance under argon atmosphere.

difference in position.

Results & Discussion

Fig. 1 displays the typical photograph of ^{10}B enriched crystal rod produced by about 5 hours at a rate of 10mm/h. From this figure, it can be found that the crystal was grown stably and the size of the present crystal was 12 mm diameter and 45 mm length on the average. The typical cross section, which was cut perpendicular to the growth direction, is shown in Fig.2. By this optical microscope observation, it was found that clear grain boundaries were not observed in the large part of the cross section. Small spots observed along straight line might indicate subgrain boundaries. At several locations of this section, $(10\bar{1}0)$ Laue patterns were obtained by using back diffraction X-ray Laue technique (Fig.3) (X-ray source ; 30 mA×30 kV). From the measurement, the crystals were found to grow normal to the <0001> of the hexagonal crystal lattice system, so that, the direction of the c-plane was the growth direction. The isotopic composition determined by GDMS analysis showed that the ^{10}B enriched crystals consisted of 93.21%^{10}B and 6.79%^{11}B and the ^{11}B enriched crystal had 99.01% ^{11}B and 0.99%1^{0}B (Table 1). From these measurements, it can be indicated that the present boron crystals are crystallographically uniform and the isotopic composition is well controlled. As for impurities, about 42 mass ppm of Mg was detected in ^{11}B crystal rod, presumably originated from MgO crucible. Although the problem of impurities remained, the growth of β-boron large bulk crystals with controlled isotopic composition was accomplished. The present isotope control of β-boron crystals will enable us to elucidate not only the nuclear properties of the two isotopes, ^{10}B and ^{11}B, but also the phonon related properties caused by the difference in mass number.

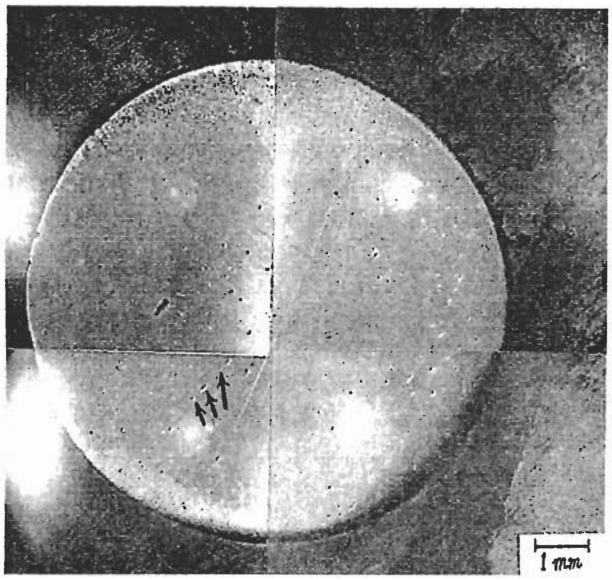

Fig.2 Photograph of the cross section of ^{10}B enriched β-B_{105} by optical microscope, perpendicular to the growth direction. Spots along the straight line were marked by arrows.

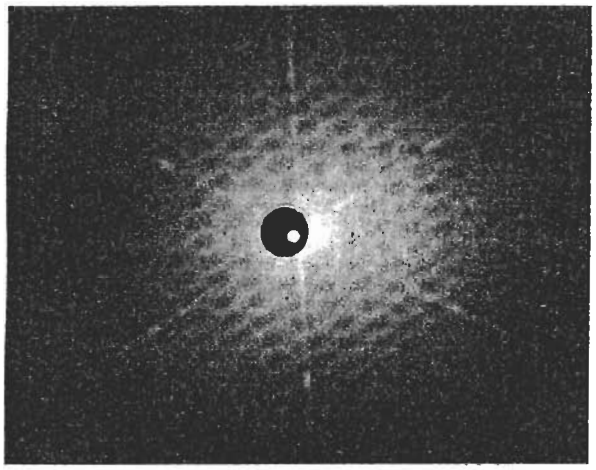

Fig.3 Laue back- reflection patterns : $(10\bar{1}0)$surface.

By using these isotopically controlled boron samples, we will study the isotope effect of thermal transport properties and their anisotropies caused by phonon mechanism of non-metals. According to the electrical transport mechanism of boron solids, electron-

Table 1 Isotopic composition of isotopically controlled boron crystals by the grow discharge mass spectroscopy (GDMS) analysis.

	^{10}B	^{11}B
^{10}B enriched	93.21%	6.79%
^{11}B enriched	0.99%	99.01%

lattice interaction are concerned with the peculiarity of the crystal structure that have cluster-like units. Therefore, the use of isotope-controlled crystals will be also fairly good for researching electron-lattice interaction of boron rich solids.

Conclusion

In the present work, we prepared large single crystals of isotopically modified β-rhom-bohedral boron (93.21%^{10}B, 99.01%^{11}B, and natural B) by the floating zone refining method. The size of the single crystal rod was 12 mm diameter and 45 mm length. It was found that the obtained crystals had few subgrain boundaries by optical microscopy and the preferential growth direction was the c-plane.

References

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