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Phonon Properties of Isotopically Modified β-Rhombohedral Boron

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We examined optical phonon and thermal transport properties of β-rhombohedral boron single crystals with different isotopic compositions (93.2% ^{10}B enriched, 99.0% ^{11}B enriched, and natural isotopic composition (19.8% ^{10}B+80.2% ^{11}B)), which were prepared by a floating zone method. The infrared-reflectance spectra of isotopically enriched ^{10}B, ^{11}B, and natural B-(β-rhombohedral B) single crystals have been measured at room temperature. For the frequency of ^{10}B, ^{11}B, and natural B, both modes of IR-active A_{2u} and E_u symmetry changed in frequency according to the inverse square root of mass number of B. The force constant was found to be slightly anisotropic for the intra-icosahedral vibrational modes between 650 and 1100 cm^{-1}. Also, the force constant for the A_{2u} mode at about 1250 cm^{-1} was comparable with the value based on the valence force model for boron carbide $B_{13}C_2$, indicating similar bond strength between pristine B and C-incorporated B. Thermal conductivity of the isotope-modified β-rhombohedral boron crystals was examined by a steady heat flow method. Temperature range of the measurement was between 5 and 130 K. At 41 K, the thermal conductivity of ^{10}B-enriched crystal was about 570 W/m · K. This is the largest value of β-rhombohedral structure and 40% larger than that of natural β-rhombohedral B crystal. The result of this thermal measurement indicated that the isotope enrichment made heat flow large because of decrease in the phonon scattering factor. © 2000 Academic Press

1. INTRODUCTION

Boron has two stable isotopes, ^{10}B and ^{11}B with the abundance of 19.8 and 80.2%, respectively. It is interesting to examine how isotope-modification affects the phonon properties (1–3). Until now, study on phonon properties with isotopically modified β-rhombohedral boron (β-rh B) single crystals (symmetry group, $R\bar{3}m$, lattice parameter: a = 1.0145 nm, $\alpha = 65°17'$) (4) has not been performed so much. The authers have been interested in the isotope effect on phonon related properties of boron because a large isotopic effect is anticipated in boron which has small mass number. Also, icosahedral boron solids have an anisotropy in the crystal structure and bonding characteristics unlike simple, for example, diamond-type structures, which makes it worth studying the isotope effect.

In the present paper, using isotope-modified and natural B crystals, we measured the infrared reflectance spectra at room temperature and the thermal conductivity at low temperature.

2. EXPERIMENTAL

2.1. Sample Preparation

Single crystal growth by floating zone (F2) melting was performed. Commercial powders, 99.5% ^{10}B enriched (ISOTEC Inc.), 99% ^{11}B enriched (ISOTEC Inc.), and natural B (Kojundo Kagaku Lab.), were used as starting materials. The raw material rods with three different isotopic compositions, ^{10}B enriched, ^{11}B enriched, and natural (19.8% ^{10}B), were prepared by powder metallurgical methods. All the single crystals were grown at the growth rate of 10 mm/h in a flowing pure argon atmosphere (flow rate is 10 L/min).

2.2. Infrared-Spectroscopic Measurement

The samples are 93.2% ^{10}B, 99.0% ^{11}B, and natural B (19.9% ^{10}B) single crystals which were prepared by zone melting (5). The (001) and (100) orientated samples were cut from the above-mentioned crystal rods. One side of the samples was polished until a mirror-like surface was obtained. Infrared reflectance spectra were measured by FTIR (JIR-7000) spectroscopy. The resolution of the measurements is 2 or 4 cm^{-1}. An aluminum mirror was used as a reference.

2.3. Thermal Conductivity Measurement

Thermal conductivity measurement was made by a steady heat flow method. The measurement was performed between liquid helium temperature and about 130 K. Heat flow is parallel to the *c*-axis. Two carbon glassy resistors were fixed on the sample at about 5-mm intervals for measuring temperature gradient.

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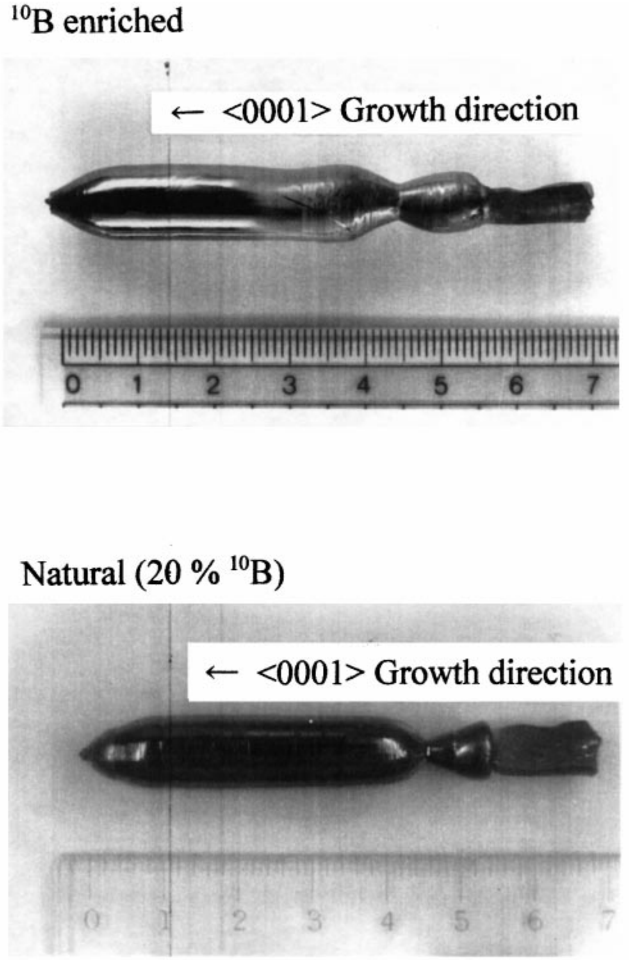

FIG. 1 ^{10}B-enriched (top) and natural (20% ^{10}B) (bottom) B crystal rods obtained by FZ melting.

3. RESULTS AND DISCUSSION

The ^{10}B-enriched and natural B crystal rods obtained by FZ melting are shown in Fig. 1. The size of the crystal rods is approximately 11 mm in diameter and 40 mm in length in average. The growth direction was parallel to the *c* axis of a hexagonal structure by an X-ray Laue method. The isotopic composition of the crystal rods analyzed by GDMS (Glow Discharge Mass Spectrometry) is shown in Table 1. Table 2 summarized the results of the analysis of impurity elements (5).

TABLE 1

	^{10}B (%)	^{11}B (%)
^{10}B enriched	93.21	6.79
$^{\mathrm{nat.}}$B	19.85	80.15
^{11}B enriched	0.99	99.01

TABLE 2

	Impurities (mass ppm)									
	C	N	O	Mg	Al	Ca	Ti	V	Fe	Ta
^{10}B 93%	290	24.6	175	0	6.3	14.2	0.2	0	0.3	0.1
$^{\mathrm{nat.}}$B	1020	3.0	16.1	3.1	4.8	4.6	2.4	0.1	1.5	0.3
^{11}B 99%	420	14.7	93.8	1.1	2.4	13.2	0.2	0.2	1.2	0.1

Infrared active phonons with the following irreducible representations are allowed at the wave vector $\boldsymbol{k} = 0$ for β-rhombohedral boron (space group, $R\overline{3}m$) (6–7):

$$\Gamma_{\boldsymbol{k}=0} = 31A_{2\mathrm{u}} + 52E_{\mathrm{u}}.$$

Figure 2 shows the imaginary parts of dielectric constant, which were obtained by Kramers-Kronig analysis of

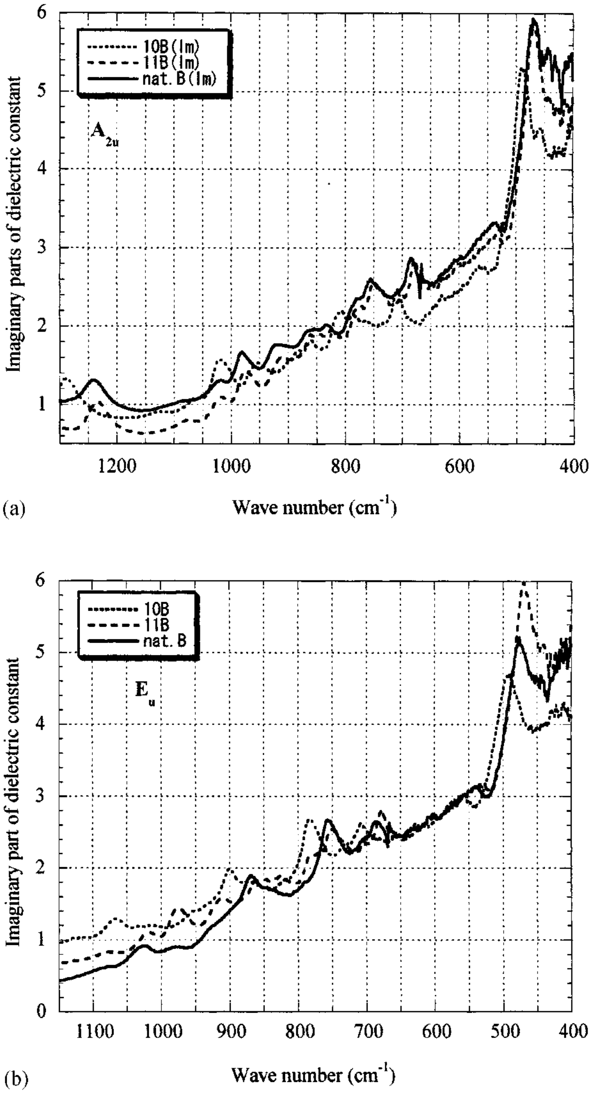

FIG. 2. (a and b) Imaginary parts of dielectric constant.

TABLE 3

A_{2u}				E_u			
^{10}B	Natural B	^{11}B	(natural B[a])	^{10}B	Natural B	^{11}B	(natural B[a])
1290	1242	1234	(1250)	1124	1082		(1090)
1166	1116	1103	(1110)	1110	1076	1070	(1050)
1125	1093	1075	(1090)	1055	1018	1009	
1062	1018	1016	(1025)				(1025)
1019	982	974	(980)	1025	980		(980)
			(940)	931	895	893	(920)
				893	860	854	
954	912	910	(925)	901	868		(865)
884	856	860	(855)	870	843	843	(830)
				783	757	747	(755)
				$\overline{731}$	$\overline{707}$	$\overline{702}$	(725)
860	825	825	(835)				
$\overline{808}$	$\overline{777}$	$\overline{776}$	(795)	708	687	(690)	
				654	633	627	(660)
786	755	748	(730)				
700	677	673	(680)				
663	646	642	(610)	627	603		(610)
				$\overline{553}$	$\overline{540}$	530	(550)
628	605	596		492		477	(475)
565	547	537	(545)	$\overline{418}$	417	$\overline{418}$	(420)
492	472	470	(472)				
457	440		(440)				

[a] Accoading to a classical dispersion theory [7].

infrared reflectance spectra of isotopially modified β-rh B. The infrared-reflectance spectra of natural B for each light polarization are in good agreement with the literature (6, 7). Table 3 shows the wave number of the infrared reflectance spectra of isotope-modified β-rh B based on a dispersion analysis (6, 7). However, it is noted that A_{2u} and E_u mode cannot be separated since using unpolarized light. It is remarkable that the modes of A_{2u} (***E***//*c*-axis) and E_u (***E***$\perp$*c*-axis) symmetry_change in frequency with different mass number of B. In the harmonic approximation, angular frequency, ω is given by

$$\omega = 2\pi ck = \sqrt{K/M_{av}}, \qquad [1]$$

where k and K are wavenumber and binding force constant, respectively. M_{av} is average mass number, $M_{av} = f_i M_{10} + (1 - f_i)\, M_{11}$, where f_i is concentration of ith isotope Figure 3 plots the experimental frequency data versus the inverse square root of the average mass. Based on the experimental value of the wave number of ^{11}B-enriched crystal, we estimated the wave number of ^{10}B by the harmonic approximation:

$$\omega_{esti.}(^{10}\mathrm{B}) = \omega_{exp.}(^{11}\mathrm{B}) \cdot \sqrt{M(^{11}\mathrm{B})/M(^{10}\mathrm{B})}$$

$$= 1.049\omega_{exp.}(^{11}\mathrm{B}) \qquad [2]$$

The experimental wavenumber of ^{10}B as a function of the inverse square root of average mass, $\sqrt{1/M}$, agreed with the predicted value. The wavenumber of natural boron (19.8% ^{10}B) was in proportion to $\sqrt{1/M}$. We considered that

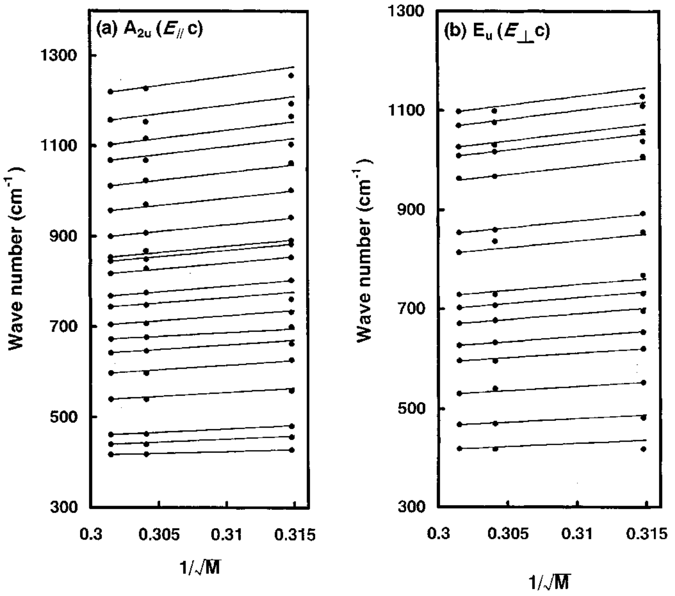

FIG. 3. Experimental frequency data vs the inverse square root of the average mass.

isotopic disorder or order effect on the phonon frequency is not significant in natural (19.9% ^{10}B) β-rh B. In addition, the force atoms in the unit cell of β-rh B, is estimated to be about 500 N/m. This is close to the value based on the valence force model for boron carbide (8, 9). This implies similar bond strength between pristine B and C-incorporated B. For the intraicosahedral vibrational mode (650–1100 cm^{-1}) originating from the Davydov splitting (10), the force constant was found to be slightly anisotropic.

Figure 4 shows the thermal conductivity, κ, vs temperature for ^{10}B(△), ^{11}B(○), and natural B(□) crystals. The data of natural boron were compared with that of Ref. (11). Heat flow is perpendicular to the c-axis. $\kappa(^{10}\mathrm{B})/\kappa(^{\mathrm{nat.}}\mathrm{B})$ is about 1.4 at 40 K. The maximum value, 570 (W/m·K) of ^{10}B-enriched crystal is the largest value in the β-rh boron. The isotope effect on thermal conductivity could be observed in the wide temperature range. The present result of thermal conductivity indicates that the isotope enrichment makes thermal conduction large because of the decrease in impurity scattering. At higher temperatures, the thermal conductivity of natural, ^{10}B and ^{11}B enriched sample showed a tendency to close. The calculated thermal conductivities by the Callaway model (12), a model of lattice thermal conductivity were also shown in Fig. 4 (dashed and dotted lines). Lattice thermal conductivity with the Debye specific heat is given by

$$\kappa(T) = \frac{k_{\mathrm{B}}}{2\pi^2 \upsilon}\left(\frac{k_{\mathrm{B}}T}{\hbar}\right)^3 \int_0^{\frac{\Theta D}{T}} \tau \cdot \frac{x^4 e^x}{(e^x - 1)^2}\,\mathrm{d}x, \qquad [3]$$

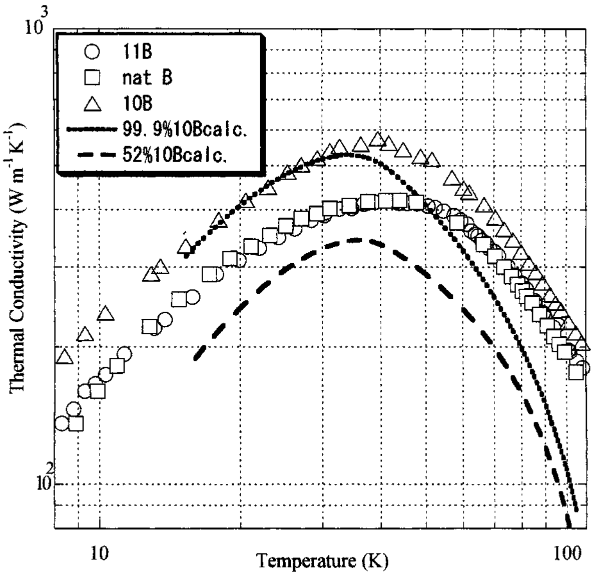

FIG. 4. Thermal conductivity, κ, vs temperature for ^{10}B, ^{11}B, and natural B crystals.

where υ and τ are the phonon velocity and relaxation time of phonon scattering, respectively. Θ_{D} is the Debye temperature. Θ_{D} of β-rh B is 1300 K. In the Callway model, the inverse of τ, the probability of scattering relaxation, is assumed as follows:

$$\tau^{-1} = (\tau_{\mathrm{grain\ \ boundary}})^{-1} + (\tau_{\mathrm{isotope}})^{-1} + (\tau_{\mathrm{phonon}^{\ddagger}\mathrm{phonon}})^{-1}$$
$$= (\upsilon/L) + A\omega^4 + e^{-1300/\alpha T}\cdot\omega^2 T^3, \qquad [4]$$

where L is the grain-boundary length. As to the second term, A, the coefficient of the impurity scattering process term can be evaluated by Klemenss postulate, $\sum_i f_i \cdot (1 - M_i/M_{\mathrm{av}})^2$. This is related to the masses variance in the crystal, which is composed of the atoms with several different masses (13). The result calculated by the Callaway model agreed with the observed value in the temperature range of impurity scattering. However, In the area of phonon–phonon scattering process (the temperature range, $T > 70$ K), the theoretical curve was not fitted so well. It might be considered that the phonon-phonon scattering of boron crystal differs from that of a simple crystal, for example, with a diamond-like crystal structure.

4. CONCLUSIONS

Single crystal growth of isotopically modified β-rh B was performed by FZ technique. The isotopic composition of the obtained crystals was controlled well.

We have measured infrared-reflectance spectra at room temperature of 93.2% ^{10}B, 99.0% ^{11}B, and natural (19.9% ^{10}B) β-rhombohedral boron. For the $A_{2\mathrm{u}}$ and E_{u} modes of ^{10}B, ^{11}B, and natural boron, which were observed with light polarization parallel or perpendicular to the c-axis, the mode frequency ω of each symmetry changed with the classical harmonic approximation.

The thermal conductivity was measured at low temperature. The obtained result showed that the isotope-enrichment of ^{10}B enhances the thermal conductivity. By using the Callaway model, we evaluate the experimental data. Around the maximum value which depends on the isotope, the calculated result agreed with the observed value.

Finally, the modification of isotopic composition of boron will provide new information on phonon related properties of icosahedral boron crystals.

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