

Peculiarities of changes of some physicochemical characteristics of monoisotopes ^{10}B , ^{11}B and natural β -boron

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Abstract

Real structure and some physicochemical characteristics of the samples of natural beta-rhombohedral boron B as well as of its ^{10}B and ^{11}B monoisotopes have been studied. It was shown that the influence of ^{10}B and ^{11}B isotopes on physicochemical properties of boron had a different character. In particular, the samples enriched with ^{11}B had high values of microhardness, shear modulus (SM) and elastic limit if compared to those of boron, while the samples enriched with ^{10}B monoisotopes were characterized with high values of thermal expansion coefficient (TEC) and thermal conductivity; lattice parameters a and c increased by the sequence: ^{11}B , B, ^{10}B . It was established that TEC, thermal conductivity, microhardness, SM and shear elastic limit increased in all samples at annealing for 5 h at 1500 °C regardless of isotope content.

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1. Introduction

Boron and boron-based compounds are being recognized as promising materials for application in the industry of semiconductors, in nuclear and reactor technique, etc. In this connection study of possibilities of changing mechanical, electro-physical, thermal, radiation and other characteristics of boron and boron-based materials becomes a question of a primary importance.

In recent years, it was shown that certain properties and characteristics of boron could be changed if boron was substituted with ^{10}B and ^{11}B isotopes. In particular, 10% difference in the mass atoms between the ^{10}B and ^{11}B monoisotopes gives the oscillation spectra different by a character of distribution of the intensities. Influence of the isotopes on properties of boron was clearly revealed in changes of thermal conductivity of boron in dependence with the isotope content. It was established that at low temperatures ($\sim 40\text{ K}$) the samples of ^{10}B monoisotopes

had higher values of thermal conductivity than those of ^{11}B monoisotopes [1]. It was also shown a possibility of changing activation characteristics of moving of structure defects such as twinning dislocations and stacking faults via changing of isotope content in the samples of β -boron [2,3]. In this connection, it was interesting to study isotopic effect on the changes of some physicochemical characteristics of β -boron.

2. Experimental

The presents study is aimed at investigating microstructure, temperature dependence of the coefficient of thermal expansion (TE), that of the absolute values of dynamic shear modulus (SM) and that of elastic limit in the samples of natural boron and its ^{10}B monoisotopes (87.8 at%) and ^{11}B (95%) monoisotopes.

All the samples for investigations were prepared on the device for floating zone melting in identical conditions. Before melting, the powders of different composition were sintered in billets and annealed for 5 h at 1900 °C in

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vacuum. The goal of annealing was to reduce carbon content in the initial samples. According to spectral analysis content of metallic impurities in the zone-melted samples was of an order of 10^{-3} at%. According to chemical analysis carbon content in B, ^{10}B and ^{11}B was 0.1, 0.15 and 0.2 mass%, respectively. Structure of the samples was coarse-crystalline.

Observations of the samples of natural boron and of ^{10}B and ^{11}B monoisotopes under transmission electron microscopy revealed polysynthetic twins and stacking faults along the planes of the $\{100\}$ system.

The procedures for TE studies were conducted on a vacuum dilatometer with inductive sensor. Measurement accuracy was 3%; heating/cooling velocity was 3°C min^{-1} . Temperature dependences of the coefficients of TE for the investigated samples are presented in Fig. 1. In the temperature range from 200 to 400°C there was observed a nonlinear increase of the thermal expansion coefficient (TEC). Deviations from the linear character of TEC had maximal meaning in ^{10}B and minimal—in ^{11}B monoisotopes. During the process of cooling there was found the TEC hysteresis with maximal meaning in the samples of ^{10}B and minimal—in ^{11}B monoisotopes.

Earlier hysteretic character of the temperature dependent TEC was found in the range of $200\text{--}500^\circ\text{C}$ in the samples of natural single-crystalline boron studied in Ref. [4]. Multiple heating/cooling cycling at temperatures from 20 to 800°C does not have any influence on the hysteretic TEC of the investigated samples. At temperatures above 600°C increase of the TEC in ^{11}B is not extensive. Increasing sequence of the values of TEC in the vicinity of 800°C is as follows: ^{11}B , B and ^{10}B . After annealing of the sample for 5 h at 1500°C the indicated sequence remains the same; hysteretic TEC at heating–cooling cycling is reduced in all samples (Fig. 2). Further multiple thermo-cycling does not have any influence on the character of TEC in the whole temperature range from 20 to 800°C .

Room-temperature microhardness measurements were carried out via using standard Vickers technique with four-

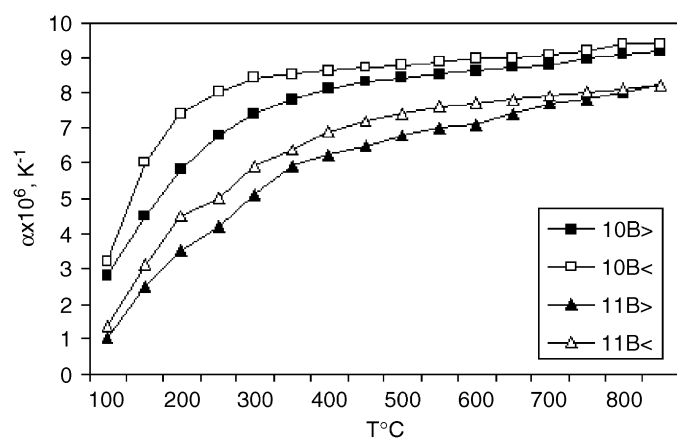


Fig. 1. Temperature dependence of the TEC of the samples of ^{10}B and ^{11}B upon heating (>) and cooling (<) in the initial state.

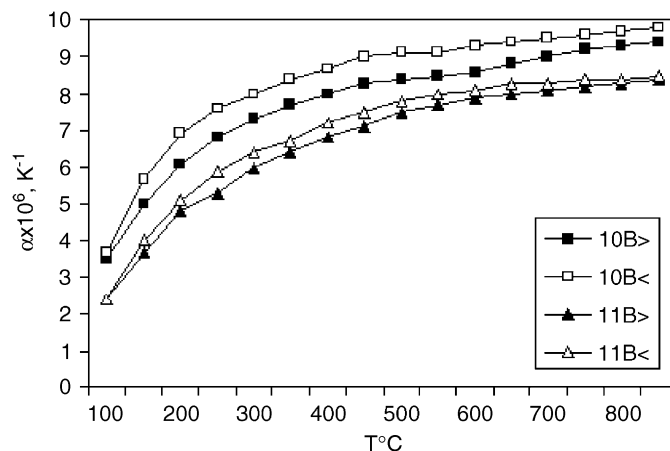


Fig. 2. Temperature dependence of the TEC of the annealed samples ^{10}B and ^{11}B upon heating (>) and cooling (<) after annealing for 5 h at 1500°C .

Table 1
Microhardness of β -boron

Samples of β -boron	Microhardness (kG mm^{-2})	
	Initial state	After annealing, 1500°C , 5 h
Monoisotope ^{10}B	4000	4250
Natural boron $^{\text{n}}\text{B}$	3850	4000
Monoisotope ^{11}B	4200	4300

faced diamond pyramid (top angle -136°) for the indentation. Loading weight was 100 g. Measurement accuracy was 3%. The results of measurements are given in Table 1. It was shown that the values of microhardness of ^{10}B and ^{11}B samples were higher if compared to those of natural boron: the top values of microhardness had the samples of ^{11}B monoisotope. Microhardness of the samples increased after high-temperature annealing at 1500°C . Differences in the values of microhardness were observed by the length of the sample. These differences were reduced after the annealing due to the relaxation of internal stresses near structural defects. Influence of isotope content on microhardness were also observed in the samples of boron carbide [5].

Measurements of room temperature thermal conductivity were carried out by stationary method in steady-state conditions. Accuracy of the measurements was 3%. It was established that the crystals of heavy ^{11}B monoisotopes had minimal thermal conductivity while thermal conductivity of the samples of ^{10}B monoisotope was rather high (see Table 2). The observed differences in thermal conductivity of the investigated samples of ^{11}B , B and ^{10}B were in a good correlation with the experimental and analytically estimated data given in Ref. [1]. Annealing of the samples for 5 h at 1500°C did not provide any significant increase to the values of thermal conductivity.

Measurements of absolute values of SM and of critical amplitudes of oscillatory deformation were carried out on a low frequency IF device with direct torsional pendulum. The samples were measured at frequencies from 0.5 to 5 Hz and at temperatures from room to 700 °C by the technique described in Ref. [6]. Velocity of the temperature change was 3 °C min⁻¹.

The values of SM and of critical amplitudes of oscillatory deformation, at which segments and kinks on dislocation defects are breaking off from the centers of pinning, are given in Table 3. There are also given the estimated data on shear elastic limit in a wide range of temperatures.

The values of absolute SM of the initial samples at different temperatures are given in Fig. 3. Sharp decrease of SM is characteristic for all the investigated samples at the temperatures ranging from 200 to 400 °C. At higher temperatures a partial recovery of the SM was observed. Decrease of the SM was maximal in the samples of ¹⁰B monoisotopes and minimal—in the samples of ¹¹B monoisotopes. Decrease of the SM is better revealed upon cooling. Annealing of the samples for 5 h at 1500 °C provides increase to the values of the absolute SM of all three samples; decay of the absolute SM in the range from 200 to 400 °C is diminished (Fig. 3). The hysteresis connected with the heating–cooling cycle is significantly reduced in the annealed samples and it is practically absent in the annealed samples of ¹¹B monoisotope.

Table 2
Thermal conductivity of β -boron

Samples of β -boron	Thermal conductivity (W K ⁻¹ cm ⁻¹)	
	Initial state	After annealing, 1500 °C, 5 h
Monoisotope ¹⁰ B	0.22	0.23
Natural boron ⁿ B	0.18	0.20
Monoisotope ¹¹ B	0.16	0.18

Table 3
Physical–mechanical characteristics of β -boron

Temperature (°C)	Shear modulus (Gpa)			Critical amplitude of deformation ($\epsilon \times 10^4$)			Shear elastic limit (Gpa)		
	ⁿ B	¹⁰ B	¹¹ B	ⁿ B	¹⁰ B	¹¹ B	ⁿ B	¹⁰ B	¹¹ B
20	170	180	195	18.0	9.0	9.5	13.6	16.2	18.5
100	160	168	180	7.7	8.0	8.4	12.3	13.4	15.12
200	75	85	100	7.2	6.8	7.5	6.37	6.78	7.50
250	55	60	70	5.8	6.2	6.5	3.1	3.72	4.55
300	45	55	60	5.2	6.0	6.2	2.34	3.40	3.72
350	50	50	60	4.8	5.4	5.8	2.40	2.70	3.48
400	60	57	65	4.3	5.0	5.3	2.58	2.85	3.44
500	75	70	80	4.0	4.7	5.0	3.0	3.29	4.00
600	80	80	95	3.8	4.4	4.6	3.04	3.52	4.37
700	85	90	100	3.6	4.1	4.3	3.06	3.69	4.30
800	90	95	110	3.5	3.9	4.1	3.15	3.70	4.50

The values of critical amplitudes of oscillatory deformation for the investigated samples are different (Fig. 4a,b): the values are low for the samples of natural boron and they are high for those of ¹¹B monoisotopes. The values of the amplitudes of oscillatory deformation increase in the annealed samples; however the sequence of increasing of their values remains unchanged: B, ¹⁰B and ¹¹B. Elastic limit was evaluated as the SM multiplied by the critical amplitude of oscillatory deformation. At room temperature measurements the sample of natural boron had the lowest meaning while the sample of ¹¹B monoisotope had the highest meaning of elastic limit.

3. Discussions

In our previous works, we have discussed the problems connected with the studies of influence of ¹⁰B and ¹¹B isotope content on the lattice parameters of β -rhombohedral boron [3]. Investigations on the influence of isotope content on the lattice parameters of boron carbide were provided in Ref. [5] and similar problems were discussed on the samples of aluminum dodecaboride in Ref. [7]. It was established that with the changes of interatomic distances

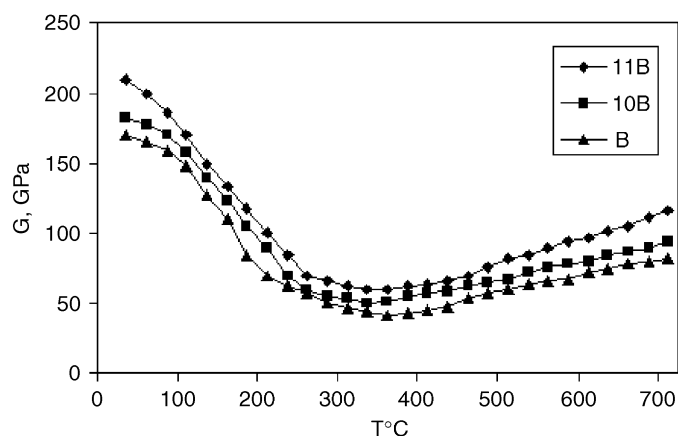


Fig. 3. Temperature dependence of the SM in the samples of natural boron B, ¹⁰B and ¹¹B monoisotopes.

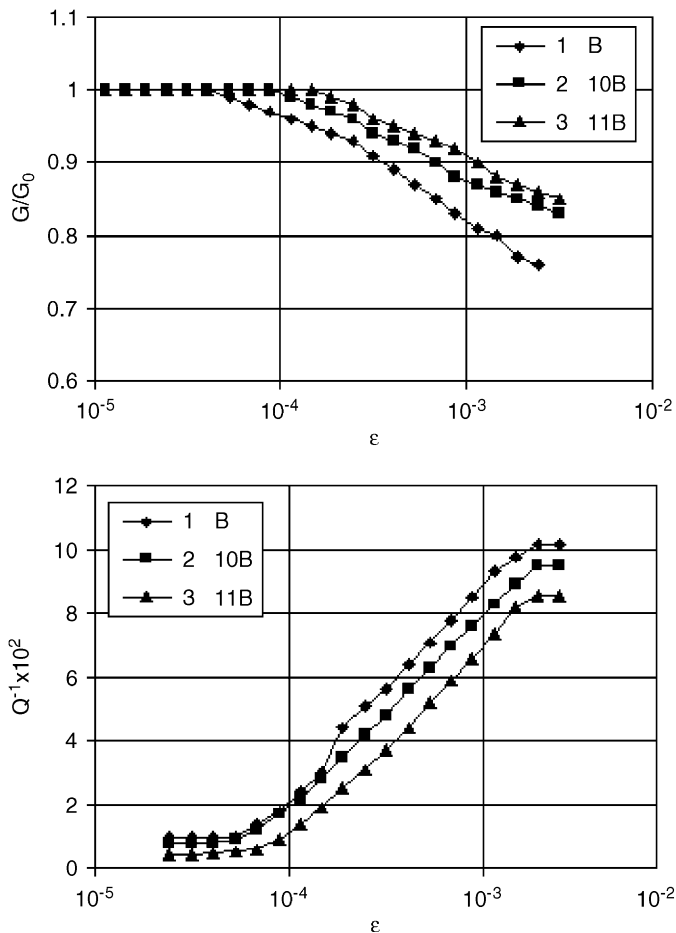


Fig. 4. Amplitude dependence of IF (a) and of relative SM (b) in the samples of natural boron B and ^{10}B and ^{11}B monoisotopes.

the lattice parameters change and these circumstances provide the observed changes of structure-sensitive properties as are: microhardness, dynamic SM, critical amplitude of oscillatory deformation and elastic limit.

The samples of B, ^{10}B and ^{11}B studied in the present work are attributed to high resistance semiconductor materials [4]. Concentration of current carriers in these materials is relatively low ($\sim 10^{17} \text{ cm}^{-3}$), therefore one can assume that transfer of energy as well as the forces of inter-atomic interactions in these samples are mainly defined by the content of the spectra of thermal oscillations, i.e. by the conditions of excitation of phonons with definite frequencies and by the group transport velocities.

Taking into account the above mentioned and basing on certain theoretical models [8] we may suppose that the observed differences in the values of TEC of the investigated samples are provided by the presence of excited phonons (different by wave length and frequencies) in the spectra of thermal oscillations at temperatures from 20 to 800 °C. In a classical harmonic approximation, angular frequencies of excited phonons are defined as $\omega = (k/M_{\text{av}})^{1/2}$ [1], where K is the force constant, $M_{\text{av}} = f_i M_{10} + (1-f_i)M_{11}$, where f_i is the concentration of the i -type isotope.

By this formula it is expected that in the case of “heavy” ^{11}B monoisotope, excitation of phonons with relatively low angular frequencies in the temperature range from 20 to 800 °C i.e. oscillations of the atoms of ^{11}B will have minimal amplitudes and hence will weakly influence on inter-atomic distances. Therefore, the value of TE of the ^{11}B crystals will be relatively low. In this connection, it may be supposed that boron crystals will occupy intermediate position between the crystals of ^{10}B and ^{11}B . The structure of natural boron consists mainly of the atoms of ^{11}B isotope ($\sim 80 \text{ at}\%$); the atoms of ^{10}B can be considered as impurity centers where the additional phonon scattering occurs [9]. In these conditions thermal action will have reducing effect on inter-atomic distances that being a reason for reducing of the values of TEC in the crystals of natural boron if compared to those of TEC in the crystals of ^{10}B . These possible changes in the phonon spectra have a reflection on the behavior of thermal conductivity in a wide range of temperatures. Discrepancies in the values of thermal conductivity and temperature dependences of the samples of monoisotopes are generally observed in the area of low temperatures [10]; however in the case of boron samples they can be revealed at room temperatures as well.

Expansion of frequency spectrum of thermally excited phonons upon diminishing of the mass of oscillating boron atom must be main reason for increasing thermal conductivity of the initial samples in the following sequence: ^{11}B , B and ^{10}B . An additional increase of thermal conductivity after high-temperature annealing may be due to decrease of the concentration of vacancies, impurities, polysynthetic twins and of stacking faults in the structure of the investigated samples. The above mentioned provides decrease of the concentration of scattering phonon centers in the lattices of all samples.

The observed increase of the values of microhardness and of SM in the samples of ^{11}B may be connected with reducing of inter-atomic distances: a tendency to reducing of the a and c parameters was experimentally revealed in the lattice of ^{11}B sample [3]. It must also be noted that low concentration of short-wave phonons can not have any noticeable weakening effect on the forces of inter-atomic interactions in the lattice of ^{11}B sample [11]. Additional increase of the indicated mechanical characteristics after high-temperature annealing can be attributed to the decrease of the density of dislocations and of polysynthetic twin boundaries that being accompanied with dissolution of impurities in the lattice and formation of localized strong electronic bonds of the sp^3 -type. As a result, the forces of inter-atomic interactions become stronger and physical-mechanical characteristics like microhardness and SM of the samples increase.

Structure of natural boron may be considered as the lattice with certain areas enriched or deficient with ^{10}B . These circumstances may induce inhomogeneous stresses enhancing mobility of dislocations as well as of deformation twins and stacking faults [12] i.e. may promote to revealing of micro plastic deformation. Such changes may

be a reason for reducing the values of elastic limit in the crystals of natural boron if compared to the crystals of ^{10}B and ^{11}B . Absence of the mass differences or the differences in atomic radiuses in the crystals of boron monoisotopes practically exclude the probability of creating inhomogeneously distributed internal stresses and promotes to better homogeneous distribution of point defects. In such cases mobility of dislocations is more efficiently constrained. These considerations can be used as an explanation for high values of the elastic limit of the ^{10}B and ^{11}B crystals. Additional increase of elastic limit under the influence of high temperature annealing by an analogy with the data described in Ref. [13] can be attributed to low density of dislocations and to strengthening effect by pinning centers.

4. Conclusions

Influence of ^{10}B and ^{11}B isotope content on thermal and structure-sensitive physical–mechanical properties of boron crystals has been studied. According to the obtained results the influence of the ^{10}B and ^{11}B isotopes on the indicated properties is attributed to the changes of phonon spectra, to the forces of inter-atomic interactions and mobility of structure defects. The results make possible to define mechanisms of changing of some characteristics of boron crystals with different content of ^{10}B and ^{11}B isotopes.

Acknowledgments

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