Peculiarities of Changes in the Structure and Structure-Sensitive Properties of Boron Isotope Crystals

D. Gabunia, L. Gabunia, O. Tsagareishvili, D. Lezhava, G. Darsavelidze, M. Antadze, M. Darchiashvili
F. Tavadze Institute of Metallurgy and Materials Science, Georgian Academy of Sciences. 15, Al. Kazbegi Ave., 0160 Tbilisi, Georgia

ABSTRACT: It has been established that the lattice parameters of ß-boron and its thermal expansion coefficient decrease with increasing of the $^{11}B/^{10}B$ ratio in boron specimens. Microhardness and absolute shear modulus are minimal for the crystals of natural boron and maximal for the crystals with maximal ^{n}B isotope content. Increase of the ^{U}B isotope content in the specimens reduces activation characteristics of the intensive IF relaxation maximum observed in natural boron in the area of 250°C, the maximum being provided by migration of twin boundaries along the {10.1} system. The obtained results are discussed in the view of possible changes in phonon spectra, the changes being provided by introduction of boron isotopes in the specimens.

1. INTRODUCTION

Resent years have been marked by a growing interest of researchers toward the effect of boron isotopes upon thermal, mechanical, electro-physical, optical and superconductive properties of boron containing materials (Karumidze et. al., 1993; Nogi et. al., 2000; Bud'ko et. al. 2001). That is why the works on investigation of the structure and structure-sensitive properties of boron crystals and those of ^{10}B and ^{U}B isotopes became more active. From this point of view, we think that study of the specimens of natural boron and of ^{10}B and ^{U}B monoisotopes obtained in identical conditions would be of a certain interest.

2. EXPERIMENT

The proposed work deals with the investigation of lattice parameters, shear modulus, thermal expansion coefficient and temperature spectra of internal friction (IF) of natural boron crystals and of their isotopes. Specimens for investigations were fabricated by melting in BN crucibles in the resistance furnace and in the installation for floating zone melting. As initial materials were used: powders of natural boron (99.5 mass%) and isotope-modified powders: ^{10}B (87.8 at.%) and ^{U}B (98.4 at.%).

X-ray diffraction analysis was conducted on a diffractometer of "flPOH-4" type with Ni filter at CuK_a radiation. Structure of the specimens under investigation was mostly coarse crystalline. On the diffraction patterns of the specimens prepared by floating zone method were sometimes found effects provided by diffraction on single crystal blocks. There were observed some differences between the sizes of crystallites and of their mutual orientation. Lattice parameters of the crystals were defined with the help of setting of conditions of X-ray shots on a diffractometer HZG-4A and scanning software of the separate diffraction maxima. The results of investigations are given in Table 1: parameter *a* of the ß-boron lattice increases together with increase of ^{10}B isotope content. At the same time, variation of ^{10}B isotope content in the specimens does not have any significant effect on the parameter c. Lattice parameters of ß-boron crystals obtained in BN crucibles in a resistance furnace practically coincide with the values given in Table 1.

Table 1. Some physical characteristics of the crystals of natural boron and of its monoisotope.

Content of lOg/llg isotopes	Lattice parameters, Â		Microhardness, kg/mm^2		CTE, lO^degree"^{1}		Shear modulus, GPa	
	a	*c*	Zone melting	Melting in BN crucibles	Zone melting	Melting in BN crucibles	Zone melting	Melting in BN crucibles
87,3/12,7	10,9480	23,7850	3700	3600	8,5	8,3	185	180
20,0/80,0	10,940	23,7846	3400	3250	8,2	8,0	175	170
5,0/95,0	10,9370	23,776	4050	3800	7,8	7,5	190	185

Microhardness of specimens at room temperature was studied on the device of "TIMT-3" type. Surface of the specimen was grinded with diamond paste with subsequent mechanical polishing. Measurements were performed under loading of 100g/mm^2. Measurement error was ±3%. Comparison of the measured results showed that the values of microhardness were higher in the specimens with ^{10}B isotope content. Specimens obtained by floating zone method were characterized by considerably high values of microhardness if compared with the specimens prepared m BN crucibles.

Measurements of relative elongation (Al/l) were performed in a vacuum dilatometer with inductive sensor at heating velocity of about 3 degree/min. Measurement accuracy was +3% (fig. 1). Increase *of* relative *elongation in the area* of 200-400°C had a non-monotonic character on the Al/l curves of the specimens prepared by floating zone method. A slight increase of relative elongation (close to linear) was observed above the temperature of 600°C. Comparison of the results of measurements-showed that the less was the ^{10}B isotope content in the specimens the less was the value of Al/l along the whole interval of temperatures. The temperature dependences for the specimens prepared in BN crucibles were analogous. Average values of a linear expansion coefficient (LEC) were estimated basing on the results obtained for a linear change of Al/l in the area of 600-800 °C. Comparison of the results (Table 1) showed that the values of LEC in zone-melted specimens were higher than those in the crucible-melted ones. The higher was the ^{10}B isotope content the higher was a value of LEC in the specimens.

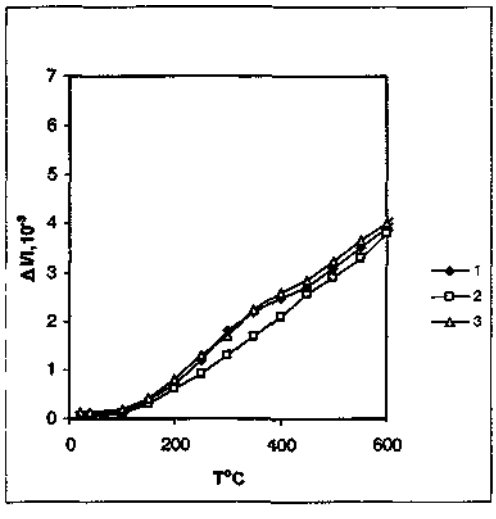

Figure 1. Temperature dependence of relative elongation Al/l of natural boron (curve 1), boron monoisotopes ^{n}B - 98.4 at.% (curve 2) and ^{10}B-87.8 at.% (curve 3).

Internal friction (IF) of the specimens was measured at frequency of 1Hz in vacuum by the method of registration logarithmic attenuation decrement of free torsion oscillations of hanging pendulum. Measurements were carried out at a heating rate of 2degree/min within the oscillation amplitude of 5-10"^{5}. Absolute value of shear modulus was defined by a method of comparison of proper oscillation frequencies of the specimen with those of the standard one. Accuracy of IF measurements was +3% and that of shear modulus was ±5%. Intense maximum at 250°C in the specimen of natural boron was observed at frequencies of ~4Hz in the IF temperature spectrum of Q"'(T) (Fig. 2). Sharp decrease of shear modulus was observed in the area of the maximum. At temperatures of 320

and 400-450°C were observed less intensive maxima in the form of kinks on the curve $Q^{-1}(T)$. Change of frequency of the specimen causes shift to the maxima at 250° and 400-450°C along the temperature axis, that proving relaxation character of the processes. Temperature of the maximum at 320°C did not depend on the oscillation frequency. Subsequently, it was of non- relaxation origin. Relaxation processes of dissipation of the energy of mechanical oscillations at 250° and at 400-450°C were characterized by activation energies of 1.3 and 2.0-2.2 eV, respectively. Corresponding values of relaxation frequency factors were 5.10^{12} and 8.10^{14} s'\ respectively.

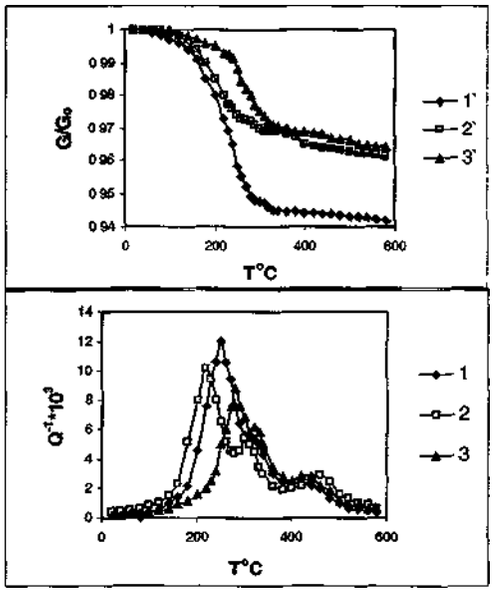

Figure 2. Internal friction spectrum Q"[1] and relative share modulus (G/G„) of natural boron (curve 1, 1*), boron monoisotopes "B-98.4 aL% (curve 2, 2') and [10]B-878 at.% (curve 3, 3') at oscillation frequency 4Hz.

IF temperature spectrum of [U]B monoisotope was characterized by the following peculiarities: maximum at 250 °C had relatively low intensity and it was shifted by 40°C to the side of low temperatures. There were observed sharp maxima on the curve $Q^{-1}(T)$ in the area of temperatures of 320 °C and 400-450°C instead of the inflections. With this, the latter maximum was shifted to the side of high temperatures by 30°C. Activation characteristics of the main maximum were significantly reduced. Maximum at 450°C was increased if compared with that of natural boron. At temperatures of the maxima shear modulus decreased proportionally to their intensities.

Relaxation and non-relaxation IF maxima of the type described above were also noted in the Q/'CT) spectrum of the specimens of [10]B monoisotope. Their intensities were comparable with the intensities of analogous IF maxima of [U]B monoisotope. However, shift of the main maximum to the side of high temperatures as well as an increase of its activation characteristics were quite detectible (Table 2).

It must be noted that the spectra of Q"'(D were thermally stable at short-term (10-30min.) as well as at long-term (5-10h) annealing at <1000°C in difference from the spectrum of *Q'(T)* of the faceted single crystals of natural boron: intensity of the maximum at 250°C in these crystals was decreasing at short-term annealing in the vicinity of temperatures of 300° and 600°C (Darsavelidze et. al., 1985).

3. DISCUSSION

In a number of papers (Tavadze at. al., 1975; Darsavelidze at. al., 1986) it was shown that relaxation processes in ß-boron were provided by mobility of the boundaries of deformation twins (250°C) and of stacking faults (400-450°C) along the {10.1} system in the stress field. It is known (Nogi et. al., 2000) that at high temperatures phonon oscillation spectra of [10]B and [U]B monoisotopes are practically identical, that being expressed in coincidence of the values of their thermal conductivity. Therefore it can be assumed that the changes of activation characteristics of the IF relaxation maxima in boron with different isotope content are not caused by peculiarities of excitation of the phonon spectra. These changes may be attributed to the changes in the sizes of crystallographic shifts of twin boundaries at 250°C and of Burgers vectors of partial dislocations and stacking faults at 400-450°C. Such a supposition was provided by the influence of isotope content on the lattice parameters observed at room temperature.

Table 2. Physical-mechanical characteristics of of natural boron and monoisotope boron crystals.

Specimens	Temperature of IF max. °C	Type of the IF maxima	Activation energy, eV	Frequency factor, c^{n}
Natural boron	250	Relaxation	1.30	$5\text{-}10^{12}$
	320	Nonrelax.		
	400-450	Relaxation	2.0-2.2	$8\text{-}10^{14}$
Monoisotope ^{10}B (87.8 at %)	270	Relaxation	1.5	$7\text{-}10^{12}$
	340	Nonrelax.		
	40	Relaxation.	1.8	$5\text{-}10^{14}$
Monoisotope ^{U}B (98.4 at %)	220	Relaxation	1.10	HO^{12}
	340	Nonrelax.		
	450	Relaxation	1.35	HO^{15}

Increase of microhardness at room temperature as well as decrease of TEC upon increasing of the ^{U}B isotope content must be connected with strengthening of inter-atomic interactions in the conditions of excitation of mostly long-wave phonons in the oscillation spectrum of ß-boron.

It was supposed (Tsagareishvili et. al., 1970) that anomalous change of Al/l in the area of 200-400°C was provided by transformations in the complexes of residual impurities interacting with planar structural defects. Therefore, we can think that one of the reasons of appearance of inflictions on the curves of Al/l at 200-400°C of natural and monoisotope boron might be rotation of separate or multiple icosahedra toward each other at continuous heating. Such processes having place in the lattice of boron were described in Ref (Shirai et. al., 1997).

The work has been supported by the ISTC, project G-402.

REFERENCES

Bud'ko S.L., Lapertot G., Petrovic C, Cunningham C.E., Anderson N., and Canfield P.C., 2001. *Boron Isotope Effect in Superconducting MgB2,* Physical Review Letters vol.86, No 9, 1877-1880.

Darsavelidze G.Sh., Tsagareishvili O.A., Tsagareishvili G.V., Tsikaridze J.N., 1985. *Internal Friction of oriented β-Rhombohedral Single crystals,* Internal Friction and Fine Structure of Metals and inorganic materials, Moscow, Nauka, 213-217.

Darsavelidze G.Sh. Tsagareishvili O.A., Eterashvih T.V., Metreveli V.Sh., Tavadze G.F., and Khomeriki D.J., 1986. *Defects and Physico-Mechanical Properties of PolicrystalUne β~ Rhombohedral Boron,* Less Common Metals, 117,189-193 (in Russian).

Karumidze G.S., and Shengelia L.A., 1993. *Isotopic Effect of Boron Carbide Thermal Conductivity,* Diamond and Related Materials. No.3., 14-17.

Nogi N., Noda T., and Tanaka S., 2000. *Phonon Properties of Isotopically Modified β-Rhombohedral Boron,* Journal of Solid State Chemistry vol.154, No.1, 296-300.

Shirai K, 1997, *The Rotation-Induced Relaxation Mechanism for Strains Application to Boron-Rich Crystals,* J. Solid State Chemistry, 133, 322-326.

Tavadze F.N., Tsagareishvili G.V., Darsavelidze G.Sh., Tavadze G.F., Khachapuridze N.A., 1975. *Relaxation Processes in Boron,* Internal Friction and Ultrasonic Attenuation m Crystalline Solids: Proceedings of the Fifth Intnational Conference, Berlin, Heidelberg, New York, Springer Velrag, 314-317.

Tsagareishvili G.V., Tavadze F.N., Khvedelidze A.G., Gabunia D.L., 1970. *Study on Some Electro-physical Properties of β-Rhombohedral Boron,* Electron Technology, Warsaw, 3,1/2, 295-299.