Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 177 (2004) 605–608
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Physical–mechanical properties of Zr-(Re)-doped β-rhombohedral boron

George Darsavelidze,[a,*] Domenti Gabunia,[a] Otar Tsagareishvili,[a] Zurab Zoidze,[a] Marina Antadze,[a] Jimsher Tsikaridze,[a] and Elgudja Kutelya[b]

[a] *Laboratory of Boron, Its Alloys and Compounds, F. Tavadze Institute of Metallurgy and Materials Science, Georgian Academy of Sciences, 15 Al. Kazbegi Avenue, Tbilisi 380071, Georgia*

[b] *Centre for Scientific Research, Georgian Technical University, 77 M. Kostava St. Tbilisi 380071, Georgia*

Received 14 October 2002; received in revised form 5 May 2003; accepted 4 July 2003

Abstract

Effect of doping with Zr(Re) on the structure and physical–mechanical properties of β-rhombohedral boron has been studied. In all specimens p-type conductivity was found. Internal friction and dynamic shear modulus of the specimens were investigated at frequencies of torsion oscillations (0.5–5 Hz) in the temperature range $80 < T < 1000$ K. The increase of Zr(Re) concentration in the samples results in increase of their hole concentration, this increasing and shifting the observed IF maxima to lower temperatures; activation energy of the maxima and frequency factor of the relaxation processes decrease by 10–15%. Effects of change of the structure-sensitive properties observed in Zr-(Re)-doped boron are analyzed in view of changes of activation energy necessary for the motion of twinning boundaries and stacking faults.

Keywords: Internal friction; Shear modulus; Activation energy; Frequency factor; Dislocations; Stacking faults; Twinning

1. Introduction

Real structure of β-rhombohedral boron is characterized with twins and stacking faults along the {100} planes [1]. Doping boron with transition metals results in increase of dislocation density [2,3]. The increase of density of defects leads to increase of carrier concentration and, as a result, of conductivity of the material [4]. In such conditions, we are given a good opportunity to study an influence of concentration of defects and electro-physical characteristics on structure-sensitive internal friction (IF) and shear modulus of boron.

It is known that characteristics of the intensive IF maxima occurring in β-boron at 530 and 570 K are changing due to doping with Zr [3], V(Ti) [5], Re [6] or Fe [7]. It was shown that doping of boron with these metals causes certain changes to the mobility of dislocation-origin defects responsible for the IF processes at 530 and 570 K.

2. Experimental

In the present work, there have been studied room-temperature electro-physical characteristics, IF temperature spectrum and shear modulus of Zr-(Re)-doped β-boron specimens. The specimens for the investigations were prepared in a high-temperature resistance furnace in vacuum. Concentration of the dopants was defined on a micro-analyzer "Camebax". Electro-physical characteristics of the specimens as well as their conductivity were established using the data on measurements of Hall coefficient and electrical conductivity in a static magnetic field. The investigated specimens exhibited hole conductivity with the hole concentration varying from 1×10^{17} to 1×10^{19} cm^{-3}. The IF and shear modulus measurements were carried out at torsion oscillations by the method described in Ref. [8]. IF spectra of B–Zr specimens were measured in the temperature range $80 < T < 1000$ K and those of B–Re specimens—in the temperature range $80 < T < 300$ K.

*Corresponding author. Fax: +995-32-370285.
E-mail address: mantadze@hotmail.com (G. Darsavelidze).

0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2003.07.009

3. Results and discussion

Table 1 shows the values of hole concentration and activation parameters of the relaxation processes. Low-temperature IF spectrum of boron doped with 0.3 at% Zr exhibits two maxima at 145 and 230 K at frequencies of ~0.5 Hz (Fig. 1, 1). At the amplitude of oscillations of about 1×10^{-5}, the maxima do not depend on the direction of temperature changes. Increase of the frequency up to 5.5 Hz causes shift of the maxima to higher temperatures. Temperatures of the IF maxima depend on frequency of oscillations, that indicate to their relaxation origin. Activation energies of the IF relaxation maxima at 145 and 230 K are 0.16 and 0.40 eV, respectively. The corresponding frequency factors are 5×10^{6} and $8\times10^{9}\,s^{-1}$. In the temperature range $80<T<300$ K, intensity of the maxima and IF background increase with the increase of room-temperature cyclic deformation where amplitude of oscillations is 5×10^{-4}, number of cycles—500. Simultaneously, the maxima shift to lower temperatures by 10–15 K. On the curve of relative shear modulus of the initial specimens (before cyclic deformation), there are observed shear modulus defects at the IF maxima; above 125 K the modulus increases up to 200 K; at temperatures from 240 to 300 K a change of the shear modulus is insignificant (Fig. 1, 1′).

Figs. 1 and 2, show that the IF maxima, observed at a frequency of ~0.5 Hz in boron doped with 0.5 at% Zr, are more intense and they shift to lower temperatures. Activation energy and frequency factor of the IF maximum at 140 K are 0.14 eV and $2\times10^{6}\,s^{-1}$, respectively. Analogous characteristics of the maximum at 225 K are reduced even to a greater extent (activation energy ~0.35 eV; frequency factor—$1\times10^{9}\,s^{-1}$).

At a frequency of ~0.8 Hz, IF spectrum of boron doped with 1 at% Zr exhibits the following changes: both maxima shift to lower temperatures; the second maximum at ~210 K significantly broadens and intensity of the background increases (Fig. 1 and 3). The background at 300 K and both IF maxima exhibit amplitude dependence. These maxima shift to the temperatures 135 and 210 K, respectively. Values of their activation energy and frequency factor reduce to 0.12 and 0.30 eV and 1×10^{6} and $8\times10^{8}\,s^{-1}$, respectively. Relative shear modulus in the vicinity of the IF maxima is also reduced (Fig. 1, 3).

In the temperature range $300<T<1000$ K at frequencies of ~1 Hz, IF spectrum of boron doped with 0.3 at% Zr exhibits intensive maxima at temperatures of 500, 540, 570 and 695 K (Fig. 2, 1). The maxima are imposed on a relatively low IF background which up to 1000 K is not temperature dependent. Intensity of the IF maxima at 570 and 695 K sharply increase with the increase of amplitude of oscillations. A position of the maximum in the vicinity of 570 K does not depend on oscillation frequency thus proving for its non-relaxation origin.

Table 1
Physical–mechanical characteristics of Zr-(Re)-doped β-boron

Materials	Hole concentration (cm^{-3}) ($T=300$ K)	Temperature of the maxima (K)	Activation energy (eV)	Frequency factor (s^{-1})	Shear modulus (GPa) ($T=300$ K)
B + 0.3 at% Zr	1×10^{17}	145	0.16	5×10^{6}	190
		230	0.40	8×10^{9}	
		500	1.10	8×10^{11}	
		540	1.30	5×10^{12}	
		695	2.00	8×10^{14}	
B + 0.5 at% Zr	5×10^{17}	140	0.14	2×10^{6}	205
		225	0.35	1×10^{9}	
		490	0.90	5×10^{11}	
		540	1.30	5×10^{12}	
		690	1.90	5×10^{14}	
B + 1 at% Zr	3×10^{18}	135	0.12	1×10^{6}	210
		210	0.30	8×10^{8}	
		475	0.85	2×10^{11}	
		540	1.30	5×10^{12}	
		685	1.80	1×10^{14}	
B + 0.3 at% Re	5×10^{17}	150	0.15	5×10^{16}	175
		235	0.40	9×10^{9}	
B + 0.5 at% Re	1×10^{18}	140	0.14	2×10^{6}	180
		230	0.35	5×10^{9}	
B + 0.8 at% Re	6×10^{18}	130	0.13	1×10^{6}	190
		230	0.30	3×10^{9}	

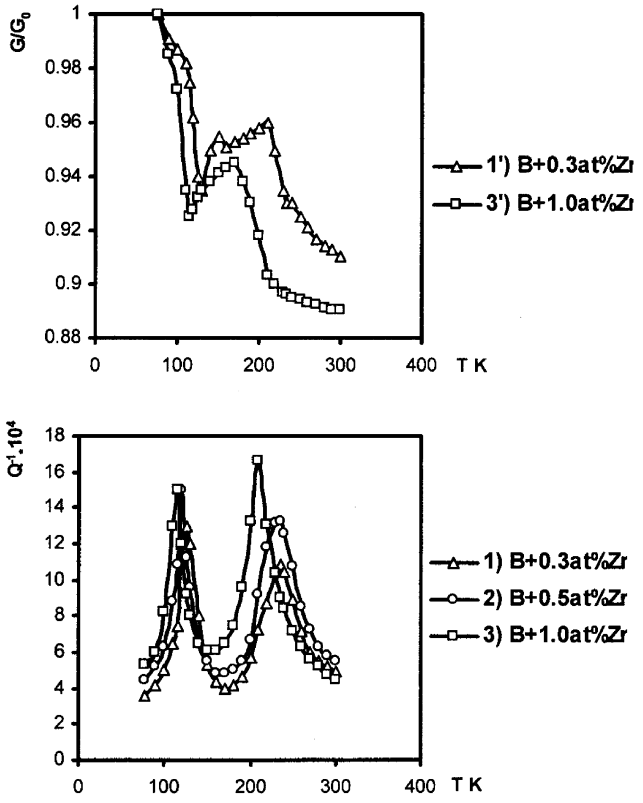

Fig. 1. Effect of doping with Zr on low-temperature IF (Q^{-1}) and on relative shear modulus (G/G_0) of β-boron.

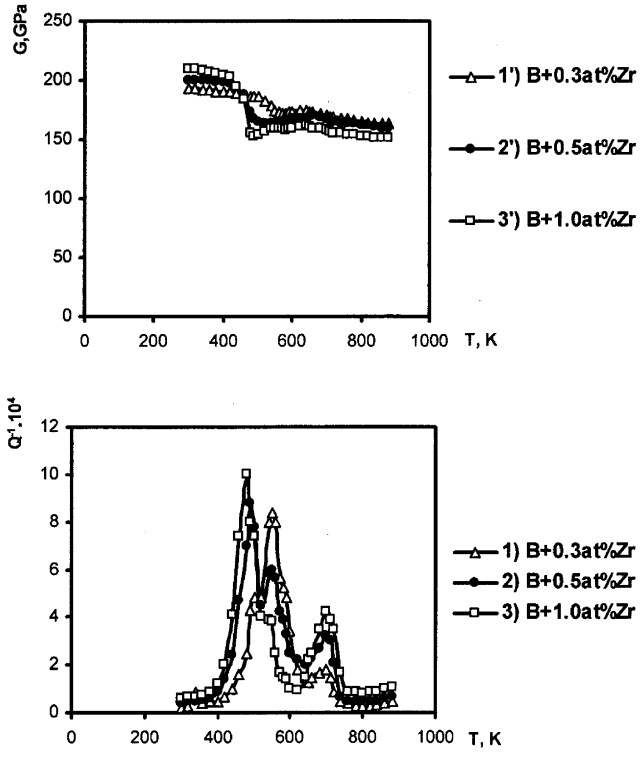

Fig. 2. Temperature dependence of IF (Q^{-1}) and shear modulus (G) of β-boron doped with Zr.

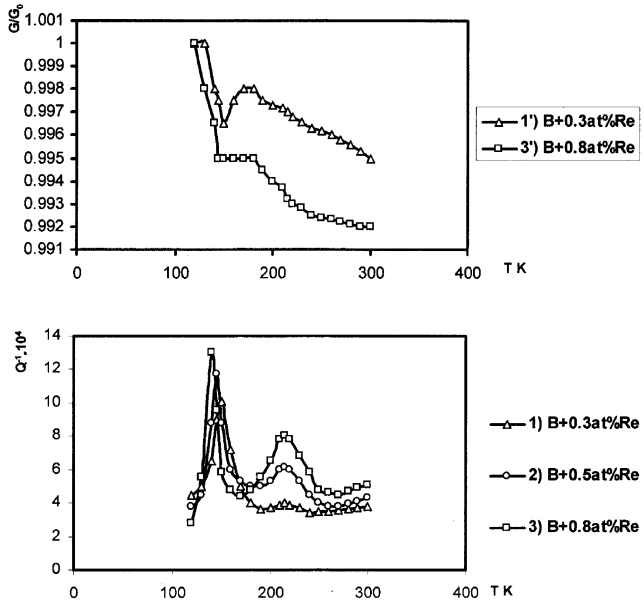

Fig. 3. Effect of doping with Re on low-temperature IF (Q^{-1}) and on shear modulus (G/G_0) of β-Boron.

Temperatures of the maxima at 500, 540 and 695 K change with the change of oscillation frequencies, i.e., these maxima have relaxation nature. The relaxation processes at 500, 540 and 695 K are characterized with activation energies 1.10, 1.30 and 2.00 eV and frequency factors 8×10^{11}, 5×10^{12}, $8\times10^{14}\,s^{-1}$, respectively.

Changes observed in the IF spectrum of boron doped with 0.5 at% Zr at frequencies of $\sim$1 Hz, are as follows: intensity of the maximum at 490 K significantly increases while that of the maxima at 540 and 570 K decreases (Fig. 2, 2). In the vicinity of 700 K, intensity of the maximum doubles. At 570 and 695 K the IF has an amplitude-dependent character.

Activation energy and frequency factor of the IF relaxation maximum at 490 K are relatively low (0.90 eV and $5\times10^{11}\,s^{-1}$, respectively). Activation energy and frequency factor of the maximum at 540 K are 1.3 eV; $5\times10^{12}\,s^{-1}$, respectively, while the same characteristics at 690 K become rather low (1.9 eV; $5\times10^{14}\,s^{-1}$, respectively).

Intensities of the IF maximum at 475 K found in boron doped with 1 at% Zr significantly increase and those of the maxima at 540 and 570 K decrease. In the vicinity of 685 K, the maximum acquires broadened and symmetric form (Fig. 2, 3). Shear modulus at the temperatures of all IF maxima significantly decreases, while with the increase of Zr concentration an absolute value of shear modulus increases (Figs. 2, 1′-3′).

In the temperature range $80<T<300$ K at frequencies of $\sim$0.8 Hz, IF temperature spectrum of boron doped with 0.3 at% Re is characterized with low maxima at 150 and 235 K. The maxima imposed on the IF background are not temperature dependent (Fig. 3, 1). Increase of the amplitude of oscillations from 1×10^{-5} to

5×10^{-4} causes increase of intensities of these maxima. At torsion oscillations of ~ 5 Hz, the maxima shift to higher temperatures by 10–15 K. Values of activation energy and frequency factor of the IF maxima are 0.15 and 0.40 eV, 5×10^{6} and $5 \times 10^{9}\,s^{-1}$, respectively. After the cyclic deformation at ~ 500 K intensities of both maxima significantly increase. Increase of intensities of the maxima is not so pronounced, after annealing of the specimens for 3 h at ~ 700 K. In the region of the IF relaxation maxima, dynamic shear modulus defects are detected (Fig. 3, 1′). Full suppression of the defects is possible after 1 h annealing at 1000 K.

Increase of the intensities of low-temperature IF maxima in boron doped with 0.5 at% Re is more evident; the first maximum shifts to lower temperatures by 10 K (Fig. 3, 2). Activation characteristic of this maximum is rather low (activation energy—0.14 eV; frequency factor—$2 \times 10^{6}\,s^{-1}$). Intensities of the maxima decrease after the specimen annealing in vacuum (10^{-3} Pa) for 1 h at 1000 K.

In the specimens doped with 0.8 at% Re, further increase of the intensities of IF maxima is observed (Fig. 3, 3); the first maximum shifts to 130 K and obtains symmetric shape. Activation energy and frequency factor of this maximum decrease to 0.13 eV and $2 \times 10^{6}\,s^{-1}$, respectively. The second maximum at 230 K is characterized by activation energy 0.3 eV and frequency factor $3 \times 10^{9}\,s^{-1}$.

Thus, our investigations show that doping of boron with Zr as well as with Re leads to decrease of activation characteristics of low-temperature maxima. However, it is interesting to note that in contrast to doping with Re [6], doping with Zr causes sharp increase to the intensity of IF maximum in the vicinity of 700 K. This effect is similar to that observed in Fe-doped boron [7].

It is known that Zr broadens boron unit cell along the trigonal axis [9]; besides, the increase of Zr concentration in boron matrix results in slightly increased electric conductivity of the material [4]. In this connection, we may suppose that significant increase of the intensity of IF maximum at 700 K as well as decrease of the value of activation energy of the relaxation processes are rather due to plastic deformation of the lattice than to any electronic effects caused by doping with Zr. Amplitude-dependent character of the IF and the observed values of their activation parameters, also presence of deformation twins and stacking faults in the structure of boron, allow us to compare these maxima with dislocation-type IF maxima observed in metals [10] and semiconductors [11]. It can also be assumed that IF maximum in the vicinity of 130–140 K may be due to the detachment of single geometrical kinks on twinning dislocations from point defects. As for the IF maximum in the vicinity of 230 K, it may be attributed to the motion of geometrical kinks on partial dislocations in local stress fields of point defects.

As a possible mechanism for the explanation of formation of the IF maximum at 500 K, a motion of twinning surface dislocations may be assumed by creating and broadening dislocation loops on the {100} planes. IF maximum at 700 K may be caused by reversible broadening of stacking faults along the {100} twinning planes. Gradual increase of the absolute value of room-temperature shear modulus in Zr-(Re)-doped boron with an increase of Zr(Re) concentration may be explained by formation of strong local bonds between atoms of boron and those of doping elements.

4. Conclusions

Electro-physical characteristics and IF temperature spectra of Zr-(Re)-doped boron have been studied. It was established that concentrations of free charge carriers increase from 1×10^{17} to $1 \times 10^{19}\,cm^{-3}$, intensities of low-temperature relaxation IF maxima increase; activation energies of these maxima decrease; appreciably decrease activation characteristics of the intense IF maxima at 500–530 and 700 K. As a possible mechanism for the explanation of low-temperature maxima, the detachment from point defects of single geometrical kinks formed on twinning dislocations is offered; for the high-temperature maxima—the motion of twinning surface dislocations ($\sim$500–530 K) and stacking faults ($\sim$700 K) in the stress field.

References

[1] M.J. Mc Kelly, A.R. Rae Smith, J. Eiring, J. Solid State Chem. 44 (1982) 374–380.
[2] G.Sh. Darsavelidze, O.A. Tsagareishvili, T.V. Eterashvili, V.Sh. Metreveli, D.J. Khomeriki, J. Less Common Met. 117 (1986) 189.
[3] G.Sh. Darsavelidze, G.V. Tsagareishvili, M.E. Antadze, O.A. Tsagareishvili, A.G. Khvedelidze, F.N. Tavadze, in: E. David, T.L. Aselage, C. Wood (Eds.), Novel Refractory Semiconductors MRS, Symposia Proceedings, Vol. 97, MRS, USA, 1987, pp. 139–144.
[4] T. Nakayama, J. Shimizu, K. Kimura, J. Solid State Chem. 154 (2000) 13–19.
[5] G.Sh. Darsavelidze, G.V. Tsagareishvili, O.A. Tsagareishvili, N.A. Khachapuridze, A.G. Khvedelidze, in: B.: Vnutrennee Trenie v issledovanii metalov, splavov I nemetalicheskix materialov Ì.: Nauka, 1989, pp. 234–239 (in Russian).
[6] G.Sh. Darsavelidze, M.E. Antadze, G.F. Tavadze, O.A. Tsagareishvili, A.G. Khvedelidze, D.N. Tsikaridze, AIP Conf. Proc. 231 (1991) 606.
[7] M.E. Antadze, Z. Zoidze, D.L. Gabunia, O.A. Tsagareishvili, D.T. Lezhava, G.Sh. Darsavelidze, J. Solid State Chem. 154 (2000) 188–190.
[8] V.S.J. Postnikov, Vnutrennee trenie v metallakh, M. ''Metallurgia'', 1974, 352pp (in Russian).
[9] B. Callmer, in: Acta Univ. Uppsal. Abstrs. Uppsala Diss. Sci., No. 434, 1977, pp. 3–48.
[10] R.R. Hasiguti, Phys. Stat. Sol. 9 (1965) 157.
[11] S.A. Antipov, V.I. Belyavskii, A.I. Drojjin, Solid State Phys. 24 (11) (1982) 3268–3272 (in Russian).