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Effect of concentrated light on morphology and vibrational properties of boron and tantalum mixtures

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Abstract

Heating a mixture of boron (impurities: carbon \sim B₅₀C₂, boric acid – H₃BO₃) and tantalum (Ta) powders in nitrogen flow in a xenon high-flux optical furnace was performed. As-received powder composed of h-BN, H₃BO₃, TaB₂, B₉H₁₁ and a number of other phases including β -rhombohedral boron, apparently, heavily doped with Ta. FT–IR examination of any sample of the material reveals the complicated vibration spectrum containing, in particular, an absorption band near 2260 cm⁻¹. The shapes of these bands are different for samples because powders were synthesized at different temperatures. Known, that in β -rhombohedral boron lattice, there are nano-sized voids of different types, which allow an accommodation of single atoms or small groups of atoms. Theoretical calculations performed by the method of quasi-classical type yields the same

value, 2260 cm^{-1} , for the vibrations frequency of Ta atoms in D-type crystallographic voids in β -rhombohedral boron lattice. Since, Ta atoms are known to prefer accommodation just in D-voids the experimentally detected bands can be identified with localized vibrations of Ta atoms.

Keywords: Condensed matter physics, Materials science, Nanotechnology

1. Introduction

The use of a concentrated solar light and high-flux xenon optical simulator for heating offers a number of significant advantages. Main features of a concentrated light are purity, practically absence of inertia of the heating, the relatively high operating temperatures (up to $2000\text{ }^{\circ}\text{C}$), the opportunity to use an effect of high temperature gradients and the ability to handle in the air, in vacuum and in the protective, oxidizing or reactive atmospheres. It is local, one-sided heating with radial symmetry of the heating zone [1, 2, 3, 4, 5].

Many methods for catalytic synthesis of BN structures [6] were developed last years. Graphite-like nanostructures including nanotubes and encapsulated polyhedral particles have been obtained by arcing hexagonal boron nitride (h-BN) and tantalum in a nitrogen atmosphere [7]. Direct synthesis of BN in nitrogen flow can be considered as a model, which allows understanding structural and phase transformation while heating in the presence of dopants. A local and one-sided heating and high temperature gradients of a xenon high-flux optical furnace defines morphology, complicated phase composition and basic physicochemical properties of powder. Therefore, this furnace can provide also conditions for transition of some of boron phases in presence of tantalum and in nitrogen flow into β -rhombohedral boron (β -B).

The β -B is a very perspective high-temperature semiconducting material [8]. Its doping mechanism can be fundamentally different from that usually occurs in conventional crystalline semiconductors. The complex crystalline structure of β -B [9] is characterized by a variety of different crystallographic voids. Thus, these nano-sized interstices can accommodate single atoms or small groups of atoms and, in particular, large metal atoms with very slight structural distortions.

The effect of doping with a number of metals on the β -B electronic structure was investigated utilizing theoretical approach of quasi-classical type [10]. Previously, the same quasi-classical method was successfully used for calculating the frequencies of atomic vibrations in diboron B_2 and some other boron-containing diatomic molecules [11], and boron nitride (BN) in different structural modifications such as hexagonal sheet [12] and nanotubes [13, 14]. The heavier dopants in β -B have to form deep donor levels inside the band gap or virtual levels inside the

valence band. Therefore, at any level of doping with these metals material has to remain semiconducting.

The frequencies of atomic vibrations associated with the same metal impurities accommodated in crystallographic voids of A-, D- and E-types characteristic of β -B lattice were calculated within the above-mentioned quasi-classical approach [15]. These vibration modes were predicted to be within the wavelength range 1080–4380 cm^{-1} , i.e. above the intrinsic phonon bands of β -B and, consequently, were attributed to localized vibrations. Therefore, metal-doping of β -B, modifying its electronic properties at the same time, can affect thermal properties of this material because metal dopants localized in nano-sized voids have to serve as additional scattering centers phonons. The detailed, but indirect, comparison of these theoretical results with experiment was carried out [16] based on the thermal conductivity measurements performed for β -B samples doped with certain metals. It was demonstrated that, the decrease in thermal conductivity in these samples indeed can be consistently explained by the mentioned scattering mechanism.

There are almost no direct experimental data on localized vibration modes of β -B crystal. Only exception is optical properties of tantalum (Ta) doped β -B studied within the range of 400–5000 cm^{-1} in [17]. An absorption band was detected near 2200 cm^{-1} . The intensity of this absorption band correlated with Ta content in tested samples, which was quite high and varied in wide range of $2 \cdot 10^{16}$ – $3 \cdot 10^{20}$ cm^{-3} . This allocation is in satisfactory agreement with the frequency of 2260 cm^{-1} calculated for vibrations of Ta atoms localized in crystallographic voids of D-type [10]. But, Ta atoms incorporated in the β -B lattice are known to occupy preferentially the D-type voids [8]. This coincidence speaks in favor of identification of vibrations of Ta atoms localized in D-type voids of β -B crystals.

Why there is the lack of optical information on impurities-related localized vibrations in β -B? It would be intelligible that, IR absorption by impurity atoms is detectable only at sufficiently high level of doping. However, according to the calculation [10] most of the dopants (Al, Co, Cr, Cu, Fe, Hf, Li, Mg, Mn, Nb, Ni, Re, Sc, Ti, V, and Zr), including Ta, introduced in the β -B lattice act as electron-donors at high concentrations leading to the “metallization” of this semiconductor and related enhancement in optical absorption associated with electron transitions. The last can mask the IR absorption by localized vibration modes.

Therefore, heating boron powder in a xenon high-flux optical furnace in a flow of nitrogen opens opportunity for formation of its new phases. Especially attention should be paid to the β -B samples doped Ta, which would have the weak effect on the IR electron transitions, for reexamining of the optical absorption in Ta-doped β -B.

2. Experimental

Boron powder with impurity of carbon of mean grain size of $0.20\ \mu\text{m}$ was selected as initial material (Fig. 1a). Phase composition of the powder was α -tetragonal boron to be stabilized by carbon impurities ($\sim\text{B}_{50}\text{C}_2$), boric acid (H_3BO_3) commonly covering fine boron particles and α -rhombohedral boron (Fig. 1b).

Heating of initial powders was carried out in a xenon high-flux optical furnace in flow of nitrogen [18]. A quartz chamber was used for new phases formation. A compacted sample of initial mixed powders boron and tantalum was placed on a surface of the compacted h-BN powder to avoid a contamination. The chamber was positioned in the center of a focal zone of three xenon emitters. Synthesis was carried out at the low density of energy in focal zone of set-up $\sim 0.7 \cdot 10^4\ \text{kW/m}^2$. Time of an experiment was 30 min. Produced powdered material was collected from copper water-cooling screens and the surface of a quartz chamber. A detailed description of the experimental can be found in [19, 20, 21, 22, 23].

Initial boron and produced powders were examined by scanning electron microscopy (SEM) “Superprobe 733” (JEOL, Japan). Crystallinity of the initial and produced powders was determined by the powder X-ray diffraction (XRD) with using diffractometer DRON–3.0 (Cu K_α radiation). It is clear that, these factors can significantly affect morphology and phase-composition of the product.

Fourier Transform Infrared (FTIR) absorption spectra were recorded by Nicolet 6700–FT–IR Fourier Spectrometer (Thermo Scientific). Absorption of the IR radiation is indicated by peaks in the spectrum, which are specific for the type of atomic vibrations in the testing material. According to the working principle, the measured intensity of the light decayed in sample is evaluated by the transmission spectra, % tm. We have converted them into absorption spectra, % abs: % abs = % 100 – % tm. The intensity of the absorptions depends upon several factors, but particularly useful information is the concentration of vibrating atoms.

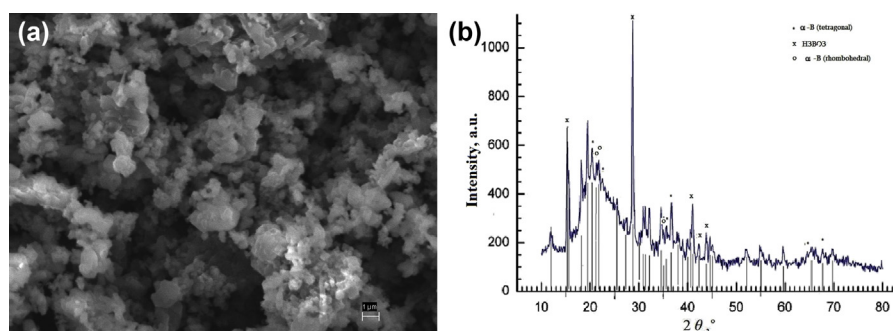


Fig. 1. SEM image of morphology (a) and XRD pattern (b) of initial boron powder (intensity in arbitrary units).

3. Results and discussion

When heated in a xenon high-flux optical furnace in flow of nitrogen mixed powders of boron and tantalum result in formation of as-received equiaxed and plate-like particles. The produced powder of a mean grain (particle) size of $\sim 1 \mu\text{m}$ that is up to 5 times larger than for initials powders. A particle size distribution was not uniform because powder was composed of two groups of particles: plate-like (a mean particle size of $2 \mu\text{m}$) and equiaxed (a mean particle size of $0.2 \mu\text{m}$), each of them has an own particle size distribution (Fig. 2a).

According XRD study, the synthesized multiphase product mainly consists of h-BN, β -B, and H_3BO_3 (Fig. 2b).

In addition, it is possible to identify traces of some other phases. Apparently, Ta reacts with excessive boron and forms boride phases, especially, tantalum diboride TaB_2 . Availability of moisture in nitrogen results in additive molecular hydrogen H_2 presence and formation not only of boron acid, but also boranes (e.g., B_9H_{11}), boron hydrides, borazine $\text{B}_3\text{N}_3\text{H}_6$, some other borane-nitrides, and also tantalum hydride Ta_2H and nitride Ta_3N_5 .

The detected crystalline phases of boron included those with chemical formulas B_{105} or B_{315} , i.e. β -B described by rhombohedral or hexagonal unit cells, respectively. Since, the powder was produced at high temperature-gradients, defective structures were formed and, as result, different complicated XRD peaks were obtained, what makes more ambiguous their identification. Their broadening and slight shift should be related, respectively, to nanocrystallinity and Ta-impurities.

Based on previous experiments [20], it can be concluded that large plate-like particles predominantly are h-BN and H_3BO_3 and, therefore, equiaxed small particles contain rest of above listed phases.

The β -B phase is obviously available in an as-received powder because in present experiments, reaction temperature was about $1200\text{--}1500 \text{ }^\circ\text{C}$. The temperature

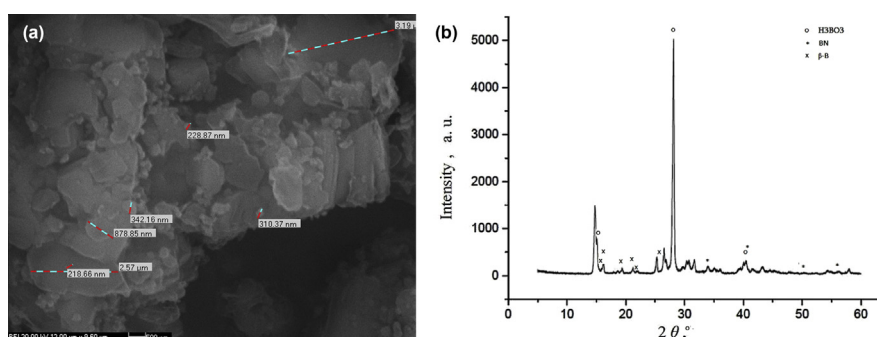


Fig. 2. SEM image of morphology (a) and XRD pattern (b) of produced powder (intensity in arbitrary units).

when α -rhombohedral boron starts its transition to the β -rhombohedral structure is at ~ 1200 °C [24].

Real content of β -B in the powdered product seems to be certainly higher than it can be seen from the XRD pattern. This assumption is supported by the detected high content of boric acid. Surface structural defects activate oxidation and hydrogenation processes in boron fine particles [25, 26] in the presence of water vapor forming boron oxide (B_2O_3) and then boric acid shell-layers (in Figs. 2b and 3 are marked only H_3BO_3 -peaks because for such multiphase mixture they are practically indistinguishable from B_2O_3 -peaks), which mask the β -B crystalline core (Fig. 3).

All the β -B component has to be heavily doped with Ta because tantalum very easily diffuses into powdered boron, especially, in presence of boron acid [27, 28].

As is known, crystalline lattices interstitial occupancies by dopants atoms can be quantitatively estimated by the XRD data if the material is characterized together with the specially prepared specimen with known composition. However, in our case it is impossible because structure of the synthesized product is too far from that of crystalline β -B:Ta. Instead, it is a multi-phase mixture containing β -B in form of nanopowder: nanocrystallinity is evident from the specific broadening of the β -B XRD peaks. On the other hand, initial charge contained up to 2 at% Ta, which is the quite enough concentration for making qualitative conclusion that the β -B phase is interstitially doped with Ta. The slight shifts of the β -B peaks positions also can be explained by impurities effect on the lattice constant.

Therefore, we can trust to the XRD analysis that product of synthesis is a mix of phases which include β -B:Ta. However, the direct experimental verification of

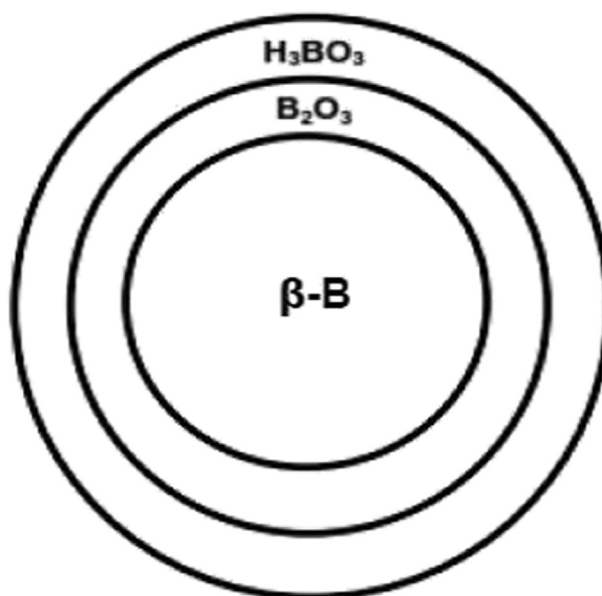


Fig. 3. Core & Shell model of fine particle of β -rhombohedral boron.

this opinion seems to be almost impossible because it is too difficult: (1) to separate β -B component from the fine-powdered multi-phase material, and (2) to remove surface shell-layers of boric acid and boron oxide which mask the β -B particles' single-phase core.

IR absorption spectra and their close-up views near peaks presumably related to the absorption by localized vibrations of Ta-impurities in β -B were obtained for samples I and II collected from the material synthesized near a reaction zone (Fig. 4a and b) and a sample III collected from the surface of a chamber wall (Fig. 4c).

FT-IR examination of each sample reveals the complicated vibration spectrum containing, in particular, an absorption band in the vicinity of 2260 cm^{-1} , theoretically predicted to be related with vibrations of Ta atoms localized in D-type subnano-sized voids of the β -B crystalline lattice. These spectra and the shapes of mentioned absorption peak are different because the samples are taken from surfaces at different distance from the focal zone, i.e. were produced at different experimental conditions, what yields the difference in phase composition.

For the samples I and II taken from the reaction zone, FT-IR spectra are quite similar each to other and peak under the consideration is placed at 2260 cm^{-1} , i.e., is undistinguishable from the value theoretically predicted in [15]. Peak heights also are close enough: 9.82 % and 8.73 %, respectively.

As for the sample III collected from the chamber wall, in general features its spectrum significantly differs from that for samples I and II. Absorption peak is broader and higher: 37.25 %. Maximum is placed at 2201 cm^{-1} . This value almost exactly

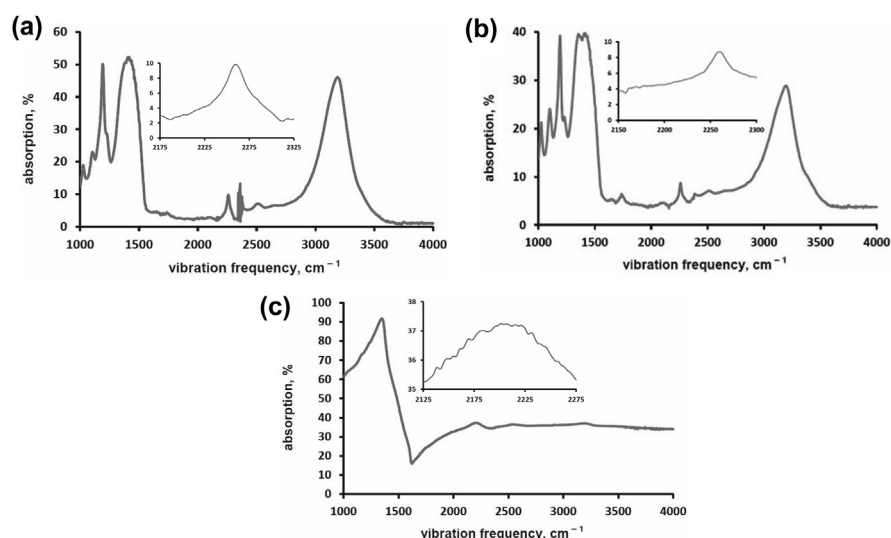


Fig. 4. FT-IR absorption spectra and their close-up views near peaks at 2260 cm^{-1} of (a) I, (b) II, and (c) III samples (axes titles in inserts are same as in figures).

coincides with the only experimental value of 2200 cm^{-1} available until now [17]. Within the errors of quasi-classical calculations, it is in agreement with theoretical vibration frequency of 2260 cm^{-1} as well.

Since, two samples were parted out from the material synthesized near the reaction zone and third sample collected from the chamber wall surface their absorption spectra differs significantly (Fig. 4). Let's emphasize that these presented spectra refer to different parts of the multi-phase product of synthesis and, consequently, they are not compatible with any spectrum known for β -B.

According to the recent review on β -B [29], there is no direct information on vibrations of metal dopants of this material. Raman spectra of numerous icosahedral boron-rich solids, including V-doped β -B, were presented in another review [30]. In addition to above mentioned theoretical study [10] of electronic parameters of metal-doped material, it was studied experimentally and analyzed an effect of some 3d-metals (Cr, Cu, Fe, Ni, and V) [31], Li and Mg [32], etc. on the β -B electronic properties and structure. There are available Raman spectra of different metal-borides: measured for LuB_{12} and ZrB_{12} [33], and numerous other dodecaborides [34] (which are excellently agreed with *ab initio* calculations of the phonon spectra); single-crystalline lanthanum hexaboride LaB_6 [35]; rare earth tetraborides REB_4 ($\text{RE} = \text{Dy}, \text{Er}, \text{Gd}, \text{Ho}, \text{La}, \text{Lu}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Tb}, \text{Tm}, \text{and Y}$) [36], etc. However, all these literature data on delocalized vibrations of metal atoms in regular lattices of metal borides are useless in case of localized vibrations of in metal-doped boron lattice. The feature detected around 2260 cm^{-1} , when it is associated with vibrations of Ta impurity atoms localized in the β -B lattice voids of D-type, cannot be directly compared with the frequency of delocalized vibrations of Ta host atoms relative to neighboring B atoms in a tantalum boride lattice.

In the β -B lattice, atoms of carbon – the main contaminator of boron – substitute boron atoms in their regular sites. As for the atoms of heavy metals, like tantalum, they can be accommodated only within the large interstitials – subnanosized crystallographic voids – characteristic for the β -B lattice. Coordination numbers of Ta-atoms placed in voids of A-, D- or E-types are high: 12, 14 and 15, respectively. Thus, if for a small part of Ta-dopants one of the nearest neighboring B-regular atoms is substituted by a C-impurity atom, this would have almost no effect on the averaged spectrum of the lattice localized vibrations.

The *ab initio*, e.g. density-functional-theory (DFT), calculations might provide convincing evidences of the β -B:Ta structural stability and the Ta-dopants' contribution in the β -B vibration spectrum. Currently, relevant theoretical studies are not available in the literature. However, calculations, previously performed by us, use quasi-classical parameterization based on the constituent atoms electronic structure obtained by *ab initio*, namely Hartree–Fock (HF), method. And these calculations have theoretically proved the experimentally already known fact that the β -B

lattice strengthens when is doped with metals. As for the accuracy of quasi-classically calculated energy-parameters, such as frequencies of lattice localized vibrations, it is estimated to be quite acceptable: less than 4 %.

In general, the vibration frequency of an atom in a solid is known to be determined by its mass and bond strength to its neighbors. At that point, we should note next:

- (1) In the relative vibrations of Ta and B atoms, the role of mass is played by the reduced mass $M_{\text{Ta-B}}$, $1/M_{\text{Ta-B}} = 1/M_{\text{Ta}} + 1/M_{\text{B}}$. Since tantalum has the significantly higher mass M_{Ta} than boron M_{B} , $M_{\text{Ta}} \gg M_{\text{B}}$, the system's reduced mass $M_{\text{Ta-B}}$ is almost undistinguishable from the mass of boron: $M_{\text{Ta-B}} \approx M_{\text{B}}$.
- (2) The mean length of a dopant atom localized in a D-type crystallographic void of the β -B lattice and surrounding boron atoms equals to 2.36 Å. This value is well-comparable with Ta–B bond lengths in tantalum borides, e.g., tantalum diboride TaB_2 – 2.38 Å. Therefore, geometric factor is one more argument why Ta atoms prefer D-voids for their accommodation. However, coordination of Ta impurities in β -B is quite different from that of Ta atoms in their regular sites of a tantalum diboride lattice: number of strong Ta–B bonds is lower and/or the weaker Ta–Ta bonds are presented as well. Ta–B bonds are expected to be stronger than B–B bonds as well from the well-known fact that, metal doping of β -B increases its strength.

Above mentioned explains why localized phonon mode of Ta-atoms doped in β -B is splitted above the band of the β -B intrinsic delocalized phonon modes.

From the obtained results we can conclude that, content of the β -B:Ta component in the powdered product is higher at lower temperature of synthesis, when more part of the initial boron is structurally transformed into β -B modification doped with Ta, but less part of initial boron is used in synthesis of BN. At higher obtaining temperatures, synthesis of boron nitride becomes more intensive reducing content of β -B phase. The β -B structure formed at higher temperatures should be more perfect, what leads to the narrowing of the Ta-related absorption peak.

4. Conclusion

Heating the mixed powders of boron and tantalum in a xenon high-flux optical furnace in flow of nitrogen results in formation of powder composed of h-BN, β -B, H_3BO_3 , and also TaB_2 , B_9H_{11} and other phases. Since heating is a local and one-sided, in presence of high temperature gradients particle size distribution is not uniform. As-received powder is composed of two groups of particles: plate-like (mainly h-BN and H_3BO_3 , a mean particle size of 2 μm) and equiaxed (β -B doped with Ta, TaB_2 , B_9H_{11} and other phases, a mean particle size of 0.2 μm), and each of them have an own particle size distribution. Tantalum very easily

diffuses into powdered boron, especially, in presence of boron acid; therefore, the β -B component is heavily doped with Ta. Partially, β -B can be hidden under H_3BO_3 layer.

Based on excellent agreement between position of the absorption peak in IR spectra of the material, containing β -B doped with Ta, experimentally detected in present work and vibration frequency of Ta atoms incorporated in β -B crystalline lattice theoretically calculated previously, we can conclude that, tantalum dopant atoms in crystalline lattice of β -rhombohedral boron predominantly occupy crystallographic voids of D-type and perform localized vibrations with frequency $\sim 2260\text{ cm}^{-1}$.

Declarations

Author contribution statement

Lina Sartinska: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Levan Chkhartishvili: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Eugen Voynich: Performed the experiments.

Ivane Murusidze: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Otar Tsagareishvili, Domenti Gabunia and Nodar Maisuradze: Analyzed and interpreted the data.

Tarik Eren and Esra Altay: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Gennadiy Frolov: Conceived and designed the experiments; Performed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] H. Lu, B.C.Y. Chan, X. Wang, H.T. Chua, C.L. Raston, A. Albu-Yaron, M. Levy, R. Popowitz–Biro, R. Tenne, D. Feuermann, J.M. Gordon, High-yield synthesis of silicon carbide nanowires by solar and lamp ablation, *Nano-technology* 24 (2013) 335603.
- [2] M.S. Payzullakhanov, Synthesis of tetragonal barium titanate in the concentrated light energy field, *Univers. J. Mater. Sci.* 1 (4) (2013) 177–179.
- [3] M.C. Hatnean, M.R. Lees, D.M.K. Paul, G. Balakrishnan, Large, high quality single-crystals of the new topological Kondo insulator, *SmB₆*, *Sci. Rep.* 3 (2013) 3071.
- [4] K. Karmakar, A. Singh, S. Singh, A. Poole, C. Rüegg, Crystal growth of the nonmagnetic Zn²⁺ and magnetic Co²⁺ doped quasi-one-dimensional spin chain compound SrCuO₂ using the traveling solvent floating zone method, *Cryst. Growth Des.* 14 (3) (2014) 1184–1192.
- [5] G. Balakrishnan, M.R. Lees, D.M. Paul, Growth of large single crystals of rare earth hexaborides, *J. Cryst. Growth* 256 (1–2) (2003) 206–209.
- [6] J. Wang, C.H. Lee, Y. Bando, D. Golberg, Y.K. Yap, Multiwalled boron nitride nanotubes: growth, properties and applications, in: Y.K. Yap (Ed.), *Lecture Notes in Nanoscale Science and Technology, B–C–N Nanotubes and Related Nanostructures*, vol. 6, Springer, New York, 2009, pp. 23–44.
- [7] M. Terrones, W.K. Hsu, H. Terrones, J.P. Zhang, S. Ramos, J.P. Hare, R. Castillo, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Metal particle catalysed production of nanoscale BN structures, *Chem. Phys. Lett.* 259 (5–6) (1996) 568–573.
- [8] L.L. Sartinska, V.S. Vorobets, G.A. Frolov, G.Y. Kolbasov, C. Jastrebski, A.Y. Koval, I.I. Timofeeva, S.V. Karpenko, Synthesis of B_xN_yC_z powder coating under concentrate light, *Vacuum* 116 (2015) 73–76. June.
- [9] D.L. Gabunia, O.A. Tsagareishvili, L.S. Chkhartishvili, G.F. Tavadze, β -Rhombohedral boron as thermoelectric material (An overview), in: I.M. Neklyudov, V.M. Shulayev (Eds.), *Nanostructural Funct. Coatings – Perspect. Mater. Nanomater, NSC KhPTI – PPC Contrast*, Kharkiv, 2007, pp. 211–272.

- [10] G.V. Tsagareishvili, M.E. Antadze, F.N. Tavadze, Producing and Structure of Boron, Metsniereba, Tbilisi, 1991.
- [11] L. Chkhartishvili, I. Murusidze, M. Darchiashvili, O. Tsagareishvili, D. Gabunia, Metal impurities in crystallographic voids of beta-rhombohedral boron lattice: binding energies and electron levels, *Solid State Sci.* 14 (11–12) (2012) 1673–1682.
- [12] L. Chkhartishvili, D. Lezhava, O. Tsagareishvili, Quasi-classical determination of electronic energies and vibration frequencies in boron compounds, *J. Solid State Chem.* 154 (1) (2000) 148–152.
- [13] L.S. Chkhartishvili, Quasi-classical estimates of the lattice constant and band gap of a crystal: two-dimensional boron nitride, *Phys. Solid State* 46 (11) (2004) 2126–2133.
- [14] L. Chkhartishvili, T. Berberashvili, I. Murusidze, On stability of small boron nitride nanotubes, in: V.E. Borisenko, S.V. Gaponenko, V.S. Gurin (Eds.), *Phys. Chem. Appl. Nanostr.*, World Scientific, Singapore, 2011, pp. 126–129.
- [15] L. Chkhartishvili, I. Murusidze, Relative stability of BN nanotubes, *Solid State Sci.* 14 (11–12) (2012) 1664–1668.
- [16] L. Chkhartishvili, I. Murusidze, Frequencies of vibrations localized on interstitial metal impurities in beta-rhombohedral boron based materials, *Am. J. Mater. Sci.* 4 (2) (2014) 103–110.
- [17] L. Chkhartishvili, I. Murusidze, Thermal conductivity of β -rhombohedral boron doped with metals in nano-sized interstitials, *Nano Studies* 7 (2013) 221–224.
- [18] O.A. Golikova, G.V. Tsagareishvili, M.M. Usmanova, T. Khomidov, D.L. Gabunia, A.S. Umarov, Z. Mirzazhonov, Impurities' effect on optical properties of β -boron, *Bull. Acad. Sci. Uzb. SSR (Ser. Phys. Math.)* (5) (1981) 88–89.
- [19] A.A. Frolov, L.L. Sartinska, Y. Koval'A, N.A. Danilenko, Application of the optical furnace for nanosized boron nitride production, *Nanomaterials* 2 (4) (2008) 115–120.
- [20] L.L. Sartinska, A.A. Frolov, A.Y. Koval, N.A. Danilenko, I.I. Timofeeva, B.M. Rud, Transformation of fine-grained graphite-like boron nitride induced by concentrated light energy, *Mater. Chem. Phys.* 109 (1) (2008) 20–25.
- [21] L.L. Sartinska, A.A. Frolov, A.F. Andreeva, A.M. Kasumov, I.I. Timofeeva, M.I. Danilenko, Catalyst-free synthesis and characterization of boron nitride whiskers and nanotubes, *Mater. Lett.* 65 (12) (2011) 1791–1793.

- [22] L.L. Sartinska, Catalyst-free synthesis of nanotubes and whiskers in an optical furnace and a gaseous model for their formation and growth, *Acta Mater.* 59 (11) (2011) 4395–4403.
- [23] L.L. Sartinska, T. Eren, E. Altay, G.A. Frolov, Effect of moisture on the boron nitride formation from elements in a xenon high flux optical furnace, *Eur. Chem. Bull.* 4 (3) (2015) 165–168.
- [24] G. Parakhonskiy, N. Dubrovinskaia, E. Bykova, R. Wirth, L. Dubrovinsky, Experimental pressure-temperature phase diagram of boron: resolving the long-standing enigma, *Sci. Rep.* 1 (96) (2011) 1–7.
- [25] D.L. Gabunia, O.A. Tsagareishvili, L.S. Chkhartishvili, Features of grinding of crystalline β -rhombohedral boron, in: A.F. Il'yushchenko, P.A. Vityaz, M.A. Andreev, V.M. Kantsevich, V.V. Savich, V.G. Smirnov, L.V. Sudnik, M.L. Khejfits (Eds.), *New Mater. Technol.: Powd. Metall. Composite Mater. Prot. Coat. Welding, Belaruskaya Navuka, Minsk, 2014*, pp. 58–61.
- [26] D.L. Gabunia, O.A. Tsagareishvili, L.S. Chkhartishvili, Z.M. Mirijanashvili, Structure and properties of β -Rhombohedral boron powders produced by mechanical grinding, *Powd. Metall. Met. Ceram.* 53 (5–6) (2014) 251–261.
- [27] F.N. Tavadze, D.L. Gabunia, G.V. Tsagareishvili, A.G. Khvedelidze, Crystalization front shape in electron-beam float-zone melting of β -B, *Inorg. Mater.* 14 (4) (1978) 665–667.
- [28] D.L. Gabunia, A.S. Umarov, M.M. Usmanova, Characters of distribution of tungsten and tantalum in β -boron crystals grown by electron-beam float-zone melting, *Inorg. Mater.* 17 (2) (1981) 252–253.
- [29] T. Ogitsu, E. Schwegler, G. Galli, β -Rhombohedral boron: at the crossroads of the chemistry of boron and the physics of frustration, *Chem. Rev.* 113 (5) (2013) 2863–3858.
- [30] H. Werheit, V. Filipov, U. Kuhlmann, U. Schwarz, M. Armbrüster, A. Leithe–Jasper, T. Tanaka, I. Higashi, T. Lundström, V.N. Gurin, M.M. Korsukova, Raman effect in icosahedral boron-rich solids, *Sci. Technol. Adv. Mater.* 11 (2010) 023001.
- [31] H. Werheit, On the exceptional negative Seebeck effect in 3d-doped β -rhombohedral boron, *Solid State Sci.* 13 (9) (2011) 1786–1796.
- [32] H. Hyodo, A. Nezu, K. Soga, K. Kimura, Self-compensation property of β -rhombohedral boron doped with high Li concentration, *Solid State Sci.* 14 (11–12) (2012) 1578–1583.

- [33] H. Werheit, Yu. Paderno, V. Filippov, V. Paderno, A. Pietraszko, M. Armbrüster, U. Schwarz, Peculiarities in the Raman spectra of ZrB_{12} and LuB_{12} single crystals, *J. Solid State Chem.* 179 (9) (2006) 2761–2767.
- [34] H. Werheit, V. Filipov, K. Shirai, H. Dekura, N. Shitsevalova, U. Schwarz, M. Armbrüster, Raman scattering and isotopic phonon effects in dodecaborides, *J. Phys. Cond. Matter* 23 (2011) 065403.
- [35] H. Werheit, V. Filipov, N. Shitsevalova, M. Armbrüster, U. Schwarz, Isotopic phonon effects in LaB_6 – LaB_6 do not possess cubic symmetry and show a non-random isotope distribution, *J. Phys. Cond. Matter* 24 (2012) 385405.
- [36] H. Werheit, V. Filipov, N. Shitsevalova, M. Armbrüster, U. Schwarz, A. Ievdokimova, V. Muratov, V.N. Gurin, M.M. Korsukova, Raman scattering in rare earths tetraborides, *Solid State Sci.* 31 (2014) 24–32. May.