

E.I. Rogacheva¹, A.N. Doroshenko¹, **V.I. Pinegin**¹, M.S. Dresselhaus²

¹National Technical University "Kharkov Polytechnic Institute",
21, Frunze Str., Kharkov, 61002, Ukraine;

²Massachusetts Institute of Technology, 77, Massachusetts Ave.,
Cambridge, MA 02139, USA

ELECTRONIC PHASE TRANSITIONS AND STRUCTURAL INSTABILITY IN $Bi_{1-x}Sb_x$ SOLID SOLUTIONS

An X-ray study of $Bi_{1-x}Sb_x$ alloys in the concentration range $x = 0 - 0.1$ was carried out. It was established that up to Sb concentration $x \sim 0.02$ the unit cell parameters (a , c) decrease linearly with increasing concentration, and the diffraction linewidth increases. In the concentration interval of $x = 0.025 - 0.1$ the $a(x)$ and $c(x)$ curves noticeably deviate from the Vegard straight line, with maximum deviations corresponding to the compositions at which the transition to a gapless state and the energy band inversion occurs ($x = 0.03 - 0.035$) and the semimetal-semiconductor transition ($x = 0.06 - 0.07$) takes place. In the indicated concentration regions, and also in the interval $x = 0.005 - 0.01$, a decrease in the X-ray diffraction line width is observed. It is suggested that the structural instability occurring in these special concentration ranges in $Bi_{1-x}Sb_x$ solid solutions is connected with changes in the electron spectrum under the percolation transition, the transition into a gapless state and band inversion and under a semimetal – semiconductor transition.

Key words: Bi-Sb solid solutions, composition, crystal structure, unit cell parameter, X-ray line width, electronic transition.

Introduction

Recently, bulk crystals of the $Bi_{1-x}Sb_x$ solid solutions and low-dimensional structures based on them have attracted much attention as promising thermoelectric and magnetoelectric materials for refrigeration devices at temperatures below ~ 200 K [1]. On the other hand, these solid solutions are interesting materials for solid state physics, because they have extremely low effective electron masses and an anomalously high charge carrier mobility and mean free-path [2-4]. Recently, interest in investigating the transport properties of $Bi_{1-x}Sb_x$ crystals and thin films has also grown sharply due to the prediction [5, 6] and subsequent experimental observation [7] of the special properties characteristic of topological insulators [5, 8] in $Bi_{1-x}Sb_x$ crystals.

Bi and *Sb* semimetal crystals are electronic analogs with a similar type of chemical bond and they crystallize under normal conditions in a similar structure (arsenic-type), which is described using not only by a rhombohedral structure but also by a hexagonal and face-centered pseudocubic lattice [9]. *Bi* and *Sb* form between themselves a continuous series of solid solutions [9].

The electronic structure of $Bi_{1-x}Sb_x$ solid solutions has been studied in a great number of works (e.g., [10-15]). In *Bi*, the *T*-valence band overlaps with the L_a conduction band at the *T*-point of the Brillouin zone. At the *L*-point, there is another valence band L_s , separated from the conduction band by a small gap (E_g). At present, it is known that with increasing *Sb* concentration, the energy difference between the L_a and L_s bands decreases, and at a certain critical concentration ($x = 0.02 - 0.04$

according to the data of different authors), a gapless state (GLS) is realized and band inversion occurs [10-15]. Then the energy difference between the L_a and L_s bands increases again. On the other hand, with increasing Sb concentration x , the T -valence band decreases in energy, and its overlap with bands at the L and T points (ΔE) vanishes for $0.06 \leq x \leq 0.07$, resulting in the semimetal-semiconductor (SMSC) transition. Due to the possibility of a radical change in the $Bi_{1-x}Sb_x$ solid solutions band structure under changing composition for this composition range, these materials are very convenient for studying peculiarities of the electronic phase transitions (EPTs) in $Bi_{1-x}Sb_x$.

In [16, 17], we reported the observation of anomalies in the isotherms of the galvanomagnetic and thermoelectric properties in $Bi_{1-x}Sb_x$ solid solutions in the concentration ranges 0.5 – 1.5, 2.5 – 3.5 and 6 – 8 at.% Sb . These peculiarities were attributed to critical phenomena accompanying the transition of a percolation type from a dilute to a concentrated solid solution, the transition to a GLS, and to the SMSC transition, respectively. Taking into account that a strong electron-phonon interaction takes place [18-20] in $Bi_{1-x}Sb_x$ solid solutions, it can be expected that a change in the electron spectrum will result in a change in the phonon spectrum, which in turn will lead to the appearance of peculiarities in the isotherms of various physical properties determined by the lattice subsystem of the crystal. In [20], for a $Bi_{0.97}Sb_{0.03}$ solid solution doped with an acceptor impurity, an increase in the high-frequency dielectric constant ϵ_∞ amounting to 30 % of the dielectric constant for bismuth ($\epsilon_\infty = 100$) was observed. The increase in high-frequency dielectric constant provides evidence for an increase in the polarizability of the valence electrons in $Bi_{0.97}Sb_{0.03}$ crystals and results from the anomalously small values of the L -point energy gap width at this composition. Due to the high polarizability of these valence electrons, the electron and lattice (phonon) properties appear to be strongly interdependent. This, in turn, causes a softening of the transverse phonon modes and an increase in the rigidity of the longitudinal modes of the optical oscillations of the crystal lattice and makes a phase transition quite possible. However, up to now, the direct observation of the suggested structural phase transitions in the $Bi_{1-x}Sb_x$ solid solutions has not been yet reported.

In this connection there arises a question, whether EPTs are accompanied by structural changes in the crystal lattice, caused by atom redistributions aimed at attaining configurations corresponding to a minimum in the potential energy.

The dependences of the unit cell parameters on the composition of the $Bi_{1-x}Sb_x$ alloys were studied in a number of works [17, 21-33]. Most authors reported a nearly linear change in the a and c parameters (of a hexagonal lattice) under changing composition over the entire concentration interval, although some authors [10, 23, 25, 26, 28] pointed out a deviation of these dependences (mainly the $c(x)$ ones) from Vegard's straight-line law. For example, in [10] a deviation from the linear dependence for the unit cell parameter c was observed for monocrystalline $Bi_{1-x}Sb_x$ alloys in the concentration range $x = 0 - 0.08$. However, according to the authors of [24], such a non-linear change was caused by the alloy inhomogeneity connected with the insufficient time of annealing (24 hours at 523 K). The authors of [31], who measured unit cell parameters along the monocrystalline ingot grown by the Chochralsky method with the concentration gradient $x = 0 - 0.18$, registered an anomalous increase in unit cell parameter c in the ingot section corresponding to $x \sim 0.07 - 0.09$. The authors, however, attributed the anomalous increase to the specificity of the growth technology.

In [17, 33], where $Bi_{1-x}Sb_x$ solid solutions in the composition ranges $x = 0 - 0.05$ [17] and $x = 0 - 0.08$ [33], annealed at 520 K for 100 [17] or 200 [33] hours were studied, it was shown that the unit cell parameters a and c decrease almost linearly as the Sb concentration increases up to $x \sim 0.02$. After that a deviation from the linear dependence, which becomes most significant near $x = 0.03$, is

observed. It was suggested that a transition to a GLS and an inversion of the valence and conduction band symmetries or they are accompanied by structural changes. However, it should have been taken into account that the duration of annealing (100 – 200 hours) could turn out to be insufficient for a complete homogenization of the samples. To rule out the influence of that technological factor, it was necessary to carry out *X*-Ray diffraction studies using samples annealed for a longer time.

The goal of the present work is performing detailed *X*-Ray studies of the $Bi_{1-x}Sb_x$ alloys after long-term annealing with a view to revealing structural instabilities connected with the existence of the EPTs.

The results of the present study have shown that GLS and SMSC transitions are accompanied by structural changes corresponding to an anomalous increase in the unit cell parameters and a decrease in the *X*-Ray diffraction linewidth (XRDL).

Experimental

Polycrystalline samples of $Bi_{1-x}Sb_x$ in the concentration range $x = 0 - 0.1$ were synthesized from high-purity elements (not less than 99.999 %) in quartz ampoules evacuated down to 10^{-3} Pa at $T = (1020 \pm 10)$ K, keeping the melt at this temperature for 5 – 6 hours. After the synthesis, the samples were quenched in air, then annealed for 720 hours at (520 ± 5) K and cooled down inside the off-powered furnace. All samples were prepared simultaneously to ensure the identity of the preparation conditions. The results of microstructural analysis showed that all prepared polycrystalline $Bi_{1-x}Sb_x$ alloys were single-phased with an average grain size $d \approx 300$ μ m. The chemical composition and homogeneity of the samples were controlled using electronic microprobe analysis (JSM-6390 LV, Jeol Ltd.), *X*-Ray photoelectronic spectroscopy using a scanning electron microscope (XPS-800 Kratos), and an *X*-ray fluorescent method. It was shown that the chemical compositions of the samples corresponded to what was intended with an accuracy of not less than 5 % (relative to one another), and the degree of the sample homogeneity was satisfactory. Additional control of the sample homogeneity, which was confirmed using the methods of measuring microhardness and microthermopower, demonstrated that the dispersion of the values of the indicated parameters within the sample did not exceed the error of their measurement.

X-ray powder diffraction studies were carried out with a DRON-2 diffractometer using *Ni* filtered *Cu K α* -radiation. The unit cell parameters *a* and *c* were determined after processing the diffraction profiles, which included smoothing, separation of the background from the reflection profiles, separation of overlapping peaks and the precise determination of their maxima location. The error in the determination of *a* and *c* amounted to $\Delta a = 2 \cdot 10^{-4}$ nm and $\Delta c = 4 \cdot 10^{-4}$ nm. The obtained values of the unit cell parameters ($a = 0.4546$ nm and $c = 1.1853$ nm) for pure *Bi* were in good agreement with those reported in other works [22-25].

Results and discussion

In Fig 1 *a*, as an example, fragments of *X*-ray diffraction patterns in the vicinity of the (0 1 14) diffraction peaks are presented for the samples with different *x* values. In Fig. 1 *b*, the dependences of the unit cell parameters *a* and *c* on the $Bi_{1-x}Sb_x$ solid solution composition, are presented. As is seen in Fig. 1 *b*, an increase in *Sb* concentration up to $x = 0.02$ leads to a practically linear decrease in both *a* and *c*, in accordance with Vegard's law. However, under further increase in *x*, in two concentration intervals: $x = 0.025 - 0.035$ and $x = 0.05 - 0.07$, the $a(x)$ and $c(x)$ curves exhibit a distinct deviation from Vegard's straight line behavior.

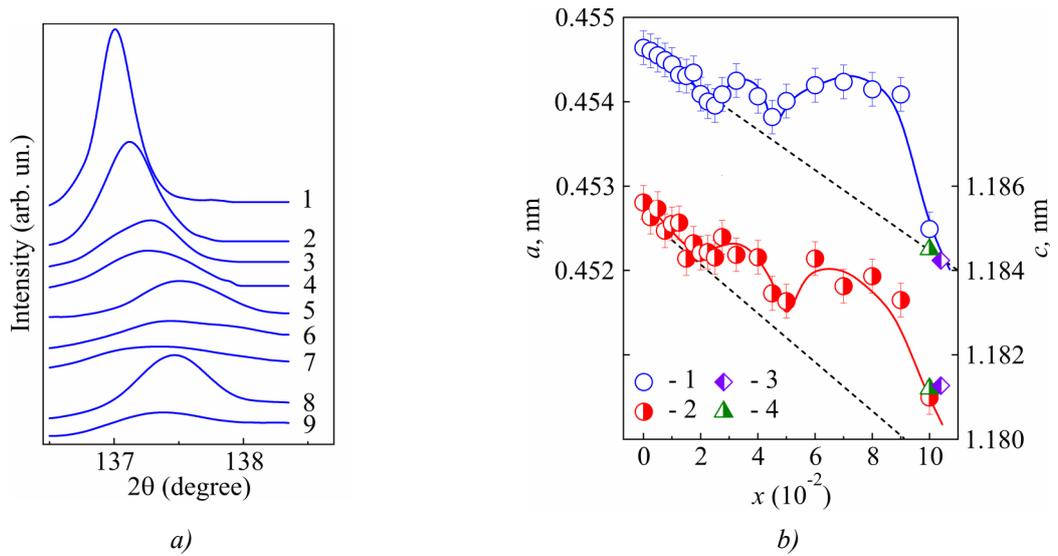


Fig. 1. Sections of the diffractograms plotting X-ray intensity vs 2θ near the (0 1 14) X-ray diffraction peaks (a), and the lattice parameters a and c (b) of the $Bi_{1-x}Sb_x$ solid solutions vs Sb concentration x : (a): $x = 0$ (1); 0.01 (2); 0.02 (3); 0.0325 (4); 0.045 (5); 0.05 (6); 0.06 (7); 0.07 (8); 0.08 (9). (b): 1 – a ; 2 – c ; 3 – data from reference [25]; 4 – data from reference [28]; line – Vegard's law.

In Fig. 2, the concentration dependences of the XRDL for the (1 4 6) reflections are presented as $\Delta B/B_0$ vs x . It is seen that the dependence has a sophisticated nonmonotonic character: in the concentration ranges $x = 0.005 - 0.01$, $x = 0.025 - 0.03$ and $x = 0.05 - 0.07$, a decrease in XRDL is observed.

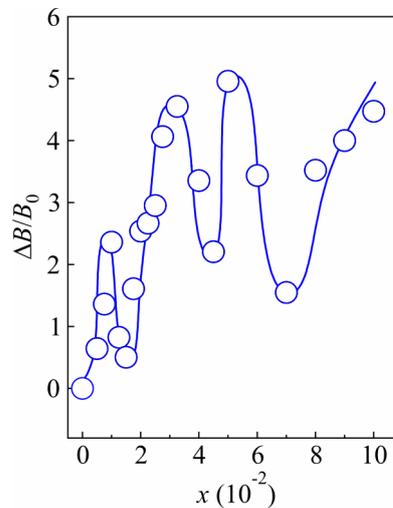


Fig. 2. The dependence of a relative change in the (0 1 14) X-ray diffraction linewidth $\Delta B/B_0$ on the Sb concentration x in the $Bi_{1-x}Sb_x$ solid solutions.

The existence of the concentration anomalies in the $a(x)$ and $c(x)$ curves provides evidence in favor of structural changes in the crystal lattice. Taking into consideration the character of these changes in the energy band structure in the $Bi_{1-x}Sb_x$ solid solutions, one can suggest that such structural changes are connected with both the transition to a GLS and the energy band inversion at the L -point of the Brillouin zone [3, 4] ($x = 0.025 - 0.035$), and with a SMSC transition ($x = 0.05 - 0.07$).

It is known that among the main factors that cause a broadening of the X-ray diffraction lines are the fluctuations of the interatomic distances due to microstresses and to the small size of the coherent scattering regions [34]. In homogeneous solid solutions, a broadening of the X-ray diffraction

lines can be caused by the disorder in the distribution of atoms of different types and the static displacement of atoms surrounding an impurity atom relative to their positions in the ideal crystal lattice. In our case the instrumental factor and the structural characteristics of the samples can be left out of consideration since for all $Bi_{1-x}Sb_x$ solid solutions, the X-ray diffraction patterns were measured under identical conditions, the same volume of material was exposed to radiation, and the degree of dispersion of the powder and the strain hardening were also the same. That is why it can be safely suggested that the change in the XRDL with changing concentration of impurity atoms can be attributed to internal structural changes.

The broadening of the X-ray diffraction lines that we observed after the introduction of the first portions of Sb atoms (Fig. 2) is easy to explain taking into account that foreign atoms introduced into the crystal increase the level of local stresses in the crystal lattice. However, the subsequent sharp decrease in the XRDL shows that in certain concentration intervals, stresses in the crystal structure decrease.

In this connection it can be suggested that in the impurity subsystem of the crystal, self-organization processes take place, resulting in the appearance of an ordered structure. Possible self-organization processes may include a long-range ordering of impurity atoms (“crystallization of the impurity liquid”) and short-range ordering (through formation of complexes). As the formation of an ordered structure must lead to lattice periodicity restoration, i.e. to a decrease in the number of defects in the crystal lattice, one should expect a decrease in XRDL, which is indeed observed in the concentration ranges $x = 0.005 - 0.01$, $x = 0.025 - 0.03$, and $x = 0.05 - 0.07$. The formation of a superstructure is expected to cause the appearance of extremum points in the dependences of different properties.

For the realization of a long-range ordering of impurity atoms, the average distance d between impurity atoms ($d = 1/n_o^{1/3}$ where n_o is the impurity atoms concentration) must correspond to their regular distribution over the sites of the crystal lattice (e.g., $d = na_o$ and $d = na_o/4^{1/3}$, respectively, for simple cubic and face-centered cubic lattices formed by impurity atoms, where n is an integer, a_o denotes the unit-cell parameter of the matrix material). If we assume the crystal lattice of $Bi_{1-x}Sb_x$ solid solutions to be a face-centered pseudocubic structure, then $a_o = V^{1/3}$, where V is the volume of the unit cell. A simple rough calculation shows that the compositions that are optimal for ordering in the case of the formation of a face-centered cubic crystal lattice of Sb atoms (i.e. compositions for which the condition $d = na_o/4^{1/3}$ is fulfilled) are close to $x = 0.01$ ($n = 4$), $x = 0.02$ ($n = 3$) and to $x = 0.07$ ($n = 2$). A sharp decrease in the XRDL, which was observed in the vicinity of the indicated compositions (Fig. 2), supports the possibility of ordering. When the solid solution region is sufficiently wide, with increasing impurity concentration, different variants of ordering can be realized. However, to prove that ordering has occurred and to determine its type, a special XRD study is required, which is beyond the scope of the present work.

In Fig. 3, along with the $a(x)$ dependence obtained in the present work for $Bi_{1-x}Sb_x$ solid solutions (Fig. 1 b), the isotherms of the magnetoresistance $\Delta\rho/\rho$ and Hall charge carrier mobility μ_H obtained at $T = 80$ K and $B = 0.9$ T in [16] are given. It is seen that the positions of extrema points near $x = 0.03$ and $x = 0.07$ in the isotherms of the lattice and electronic properties are practically similar. Let us also notice that the anomaly in the range $x = 0.005 - 0.01$ observed in [16] for the electronic properties and in the present work for the X-ray diffraction line width, is not observed for the unit cell parameters. This observation indicates that the formation of percolation channels, significantly affecting the transfer phenomena and the X-ray diffraction line width, does not cause noticeable changes in the unit cell parameters.

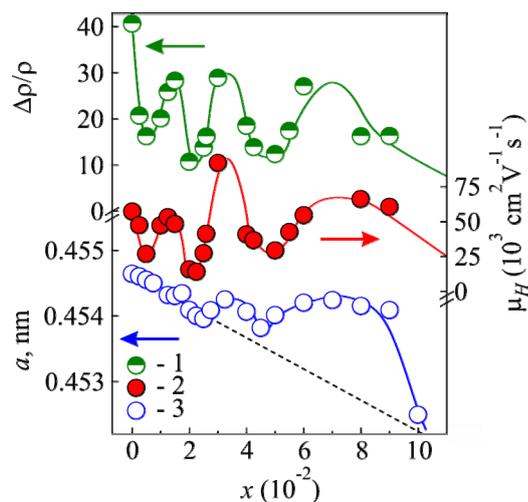


Fig. 3. The dependences of the magnetoresistance $\Delta\rho/\rho$ (1), Hall charge carrier mobility μ_H (2), and unit cell parameter a (3) on the Sb concentration x of $Bi_{1-x}Sb_x$ solid solutions at room temperature. Here (1), (2) refer to [16], and (3) to the present work.

Thus, it follows from the obtained data that the electronic phase transitions occurring in the studied range of concentrations are accompanied by the processes of structural ordering. The latter are manifested through the sharp narrowing of XRD and the deviation from Vegard's law in the concentration intervals where extrema of electronic properties are observed. At present it is difficult to say which factor – electronic or structural – is primary in determining the appearance of the concentration anomalies of properties in $Bi_{1-x}Sb_x$ solid solutions, as in crystals the electronic and lattice subsystems are closely connected and can be considered independent only conventionally. One should not also exclude that for each of the critical concentration ranges ($x = 0.005 - 0.01$, $x = 0.025 - 0.03$ and $x = 0.05 - 0.07$) there exist two phase transitions – electronic and structural – which occur at close compositions.

Conclusions

For the first time it is here established that in $Bi_{1-x}Sb_x$ solid solutions in the concentration range $x = 0 - 0.1$, the dependences of the unit cell parameters and X-ray diffraction line widths on the Sb concentration exhibit a distinct non-monotonic oscillatory behavior: in the vicinity of compositions $x = 0.03$ and $x = 0.07$, the maximum positive deviations from Vegard's law are observed, and in the vicinity of compositions $x = 0.01$, 0.03 , and 0.07 , a narrowing of the X-ray diffraction lines takes place. The results obtained show that electronic phase transitions (a transition of a percolation type to impurity continuum, a transition to a gapless state accompanied by L-point inversion and by a semimetal-semiconductor transition), occurring in the same concentration intervals, are accompanied by structural changes in the crystal lattice, presumably connected with the formation of ordered structures. This, in turn, indicates a strong electron-phonon interaction in $Bi_{1-x}Sb_x$ solid solutions.

Acknowledgement. The authors thank Dr. Olga Naschekina and Shuang Tang for fruitful and stimulating discussions. This work was supported by the Ukrainian State Foundation for Fundamental Research (grant № UU 42/006-2011) and by the CRDF grant № UKP2-7074-KK-12. The MIT author acknowledges support from grants № NSF/DMR-1107339 and № RF01224242.

References

1. D.M. Rowe, *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, London, New York, Washington, 1995).
2. V.S. Edelman, Electrons in Bismuth, *Adv. Phys.* **25** (6), 555 – 613 (1976).
3. B. Lenoir, M. Cassart, J.-P. Michenaud, H. Scherrer, and S. Scherrer, Transport Properties of Bi-Rich Bi-Sb Alloys, *J. Phys. Chem. Solids* **57** (1), 89 – 99 (1996).
4. A. Banerjee, B. Fauqué, K. Izawa, A. Miyake, I. Sheikin, J. Flouquet, B. Lenoir, and K. Behni, Transport Anomalies Across the Quantum Limit in Semimetallic $Bi_{0.96}Sb_{0.04}$, *Phys. Rev. B* **78**, 161103 (2008).
5. L. Fu, C.L. Kane, and E.J. Mele, Topological Insulators in Three Dimensions, *Phys. Rev. Lett.* **98**, 106803 (2007).
6. S. Murakami, Phase Transition Between the Quantum Spin Hall and Insulator Phases in 3D: Emergence of a Topological Gapless Phase, *New Journal of Physics* **9**, 356 – 372 (2007).
7. D. Hsieh, D. Qian, L. Wray, Y. Xia, Y.S. Hor, R.J. Cava, and M.Z. Hasan, A Topological Dirac Insulator in a Quantum Spin Hall Phase, *Nature* **452**, 970 – 974 (2008).
8. J.E. Moore and L. Balents, Topological Invariants of Time-Reversal-Invariant Band Structures, *Phys. Rev. B* **75**, 121306 (2007).
9. Ya.A. Ugay, E.G. Goncharov, G.V. Semenova, and V.B. Lazarev, *Phase Equilibrium between Phosphorus, Arsenic, Antimony and Bismuth* (Nauka, Moscow, 1989).
10. A.L. Jain, Temperature Dependence of the Electrical Properties of Bismuth-Antimony Alloys, *Phys. Rev.* **114** (6), 1518 – 1528 (1959).
11. N.B. Brandt, S.M. Chudinov, and V.G. Karavaev, The Study of the Gapless State, Induced by the Magnetic Field in Bismuth-Antimony Alloys, *Zh. Eksp. Teor. Fiz.* **70** (6), 2296 – 2317 (1976).
12. E.E. Mendez, A. Misu, and M.S. Dresselhaus, Pressure Dependent Magnetoreflexion Studies of Bi and $Bi_{1-x}Sb_x$ alloys, *Phys. Rev. B* **24** (2), 639 – 863 (1981).
13. E.J. Tichovol'sky and J.G. Mavroides, Magnetoreflexion Studies on the Band Structure of Bismuth-Antimony Alloys, *Solid State Commun.* **7**, 927 – 931 (1969).
14. R. Herrmann, W. Braune, and G. Kuca, Cyclotron Resonance of Electrons in Semimetallic Bismuth-Antimony Alloys, *Phys. Stat. Sol. (b)* **68** (1), 233 – 242 (1975).
15. W. Braune, G. Kuka, H.J. Gollnest, and R. Herrmann, Microwave Spectroscopy in Semimetallic Bismuth-Antimony Alloys, *Phys. Stat. Sol. (b)* **89** (1), 95 – 101 (1978).
16. E.I. Rogacheva, A.A. Drozdova, and M.S. Dresselhaus, *Proc. Conf. Thermoelectrics* (July-August 2006, Vienna, Austria), ISSN 1094-2734, p. 107 – 110.
17. E.I. Rogacheva, A.A. Yakovleva, V.I. Pinegin, and M.S. Dresselhaus, Concentration Anomalies of Properties in Bi-Sb Semimetallic Solid Solutions, *J. Phys. Chem. Solids* **69** (2), 580 – 584 (2008).
18. I.L. Yarnell, I.L. Warren, R.G. Wenzel, and S.H. Koenig, Phonon Dispersion Curves in Bismuth, *J. Res. Dev.* **8** (3), 234 – 240 (1964).
19. J. Sosnowski, S. Bednarski, W. Bühner, A. Czachor, and E. Maliszewski, Phonon Dispersion Relations in the $Bi_{0.95}Sb_{0.05}$ Alloy, *Phys. Stat. Sol. (b)* **104** (1), 97 – 102 (1981).
20. N.P. Stepanov, Plasmon-Phonon Polaritons in an Acceptor Impurity-Doped Bismuth-Antimony Crystals, *Semiconductors* **38** (5), 552 – 555 (2004).
21. E.G. Bowen and W. Morris-Jones, X-ray Investigation of the Bismuth-Antimony, *Philosophical Magazine Series 7*, **13** (87), 1029 – 1032 (1932).
22. W.F. Ehret and M.B. Abramson, The Nature of the Solid Phase in the System Antimony-Bismuth. *J. Am. Chem. Soc.* **59** (2), 385 – 388 (1934).

23. R. Cucka and C.S. Barrett, The Crystal Structure of *Bi* and Solid Solutions of *Pb*, *Sn*, and *Te* in *Bi*, *Acta Crys.* **15** (9), 865 – 872 (1962).
24. M. Dugue, Proprietes Electriques des Solutions Solides Bismuth-Antimoine *Phys. Stat. Sol.* **11**, 149 – 158 (1965).
25. J.P. Dismukes, R.J. Paff, R.T. Smith, and R.J. Ulmer, Lattice Parameter and Density in Bismuth-Antimony Alloys, *Chemical and Engineering Data* **13** (3), 317 – 320 (1968).
26. V.J. Meisalo, Lattice Parameters of *Bi-Sb* Alloys at 4.2 K, *Applied Crystallography* **3** (2), 224 – 228 (1970).
27. N. Wagner and O. Brümme, Remarks on the Relation between Crystal Structure and Electronic Band Structure in Bismuth-Antimony Alloys, *Phys. Stat. Sol. (b)* **75**, K 157 – 161 (1976).
28. H. Berger, B. Christ, and J. Troschke, Lattice Parameter Study in the $Bi_{1-x}Sb_x$ Solid-solution System, *Crystal Research and Technology* **17** (10), 1233 – 1239 (1982).
29. U. Pietsch, The Validity of Vegard's Rule for the Solid Solution System $Bi_{1-x}Sb_x$, *Phys. Stat. Sol. (b)* **110** (1), K5 – K9 (1982).
30. R. Martin-Lopez, B. Lenoir, X. Devaux, A. Daucher, and H. Scherrer, Mechanical Alloying of BiSb Semiconducting Alloys, *Mater. Sci. Eng. A* **248**, 147 – 152 (1998).
31. G.N. Kozhemyakin, D.V. Lutskiy, M.A. Rom, and P.V. Mateychenko, Growth of Sb_xBi_{1-x} Gradient Single Crystals by the Czochralski Method with *Bi* Feed, *J. Crystal Growth* **311**, 1466 – 1470 (2009).
32. J. Druzek, Positron Preferential Annihilation in *Bi-Sb* Alloys, *Phys. Stat. Sol. B*, **246** (10), 2238 – 2241 (2009)
33. A.N. Doroshenko, A.A. Drozdova, V.I. Pinegin, and E.I. Rogacheva, X-ray Study of Bismuth-Antimony Solid Solutions, *Scientific Bulletin of Uzhgorod National University, Ser. Physics*, **30**, 107 (2011)
34. Ya.S. Umanskii, *X-Ray Study of Metals and Semiconductors* (Moscow: Metallurgiya, 1969), p. 38.

Submitted 26.11.2013.