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Thermoelectric Efficiency of Bi-Sb and Bi-Se Based Thermoelements

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Abstract: The article discusses the properties of solid solutions based on bismuth and antimony, which are considered the best thermoelectric materials for the low temperature range. The improvement of the conversion efficiency in thermoelectric materials is primarily due to the increase in the efficiency coefficient (Z), which can be achieved by forming solid solutions of semiconductor materials. Graphs related to thermoelectric power, electrical conductivity, and mobility of charge carriers in the alloy are presented.

Key words: single crystal, stoichiometry, chalcogenide, halide, thermal conductivity, mobility, thermoelectricity, degeneracy.

Introduction

In order to obtain Z values of the thermoelectric efficiency of the solid solution, 3-4 times more tellurium is added to its composition. The action of the excess tellurium is to suppress the receptive force of the excess antimony formed due to the shift in stoichiometry. As a result, in the solid solution containing 74 mol % Sb_2Te_3 - 26 mol % Sb_2Te_3, the value of Te impurity grown from solution is (Z=3÷3.3). It should be noted that excess tellurium does not dissolve, but is released as a second phase, which also affects the efficiency of the material.

Among n-type materials, alloys based on $Bi_2Te_3 - Bi_2\,Se_3$ solid solutions containing $Bi_2\,Se_3$ alloyed with 4-10 mol % halides have the highest efficiency have. The maximum thermoelectric efficiency of these materials is achieved at room temperature and is (2,9÷3,0) 10^{-3} 1/K.

The studied alloys have a strong anisotropy of properties, so the properties of their polycrystals depend on the degree of grain misorientation. In addition, the complexity of obtaining alloys based on $\mathrm{A}_2^{\mathrm{V}}\mathrm{B}_3^{VI}$compounds is that they crystallize with a significant deviation from stoichiometry. This results in the concentration of carriers in bulk samples obtained from stoichiometric solution being significantly higher than the optimal concentration corresponding to the maximum efficiency of the material.

A number of articles and monographs are devoted to the study of solid solutions based on antimony and bismuth chalcogenides. Here are the results of some of them published in recent years. The main direction of these studies is aimed at increasing the thermoelectric efficiency of bismuth and antimony chalcogenides.

Materials and methods

It was found that the Bi atoms in the compound Bi_2Te_3 are located in the selenium sub-lattice under certain synthesis conditions and behave as singly ionized acceptors: atoms $Bi_{1-x}\mathrm{Te}_{\mathrm{x}}$ (x = 0,005 ÷ 0,05) and $Bi_{0,88}Se_{0,12}$, , for Te (x=0,001÷0,05), changes the energy spectrum, thereby changing the conductivity value [5].

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Simultaneous introduction of Sb, Se and S atoms into solid solutions of the type $Bi_{2-z}Sb_zTe_{3-x-y}$ in the concentration range 0≤x±y≤9(x). /y-1) and 0<z<0.6 leads to an additional decrease in lattice thermal conductivity [6]. The addition of $\mathrm{Bi_2Te_3-Sb_2Te_3}$ solid solution to Sb_2Se_3 allows to significantly reduce the thermal conductivity of the lattice and practically does not affect the scatter. charge carriers. Lead impurity is an acceptor and increases the concentration of positive current carriers in the solid solution of $Sb_{1,5}\mathrm{Bi}_{0,5}Te_3$ With the introduction of an element in the amount of up to 0.1 atm%, each atom doubles the concentration of holes. When lead is combined with tellurium, each of its atoms gives one or less current carriers [3].

$Sb_{1,425}Bi_{0,575}Te_3Se_{0,15}$to study the effect of electroactive germanium and copper mixtures on thermoelectric properties of solid solution [7]. Doping the initial solution at 300 K leads to an increase in the concentration of current carriers, an increase in electrical conductivity and a decrease in thermoEMF.

In order to reduce the concentration of impurity current carriers and to study the properties in the internal conductivity region, we used the method of introducing alloys $Sb_{1-x}Bi_x\mathrm{Te}_3$ $(x = 0 \div 1)$. extrusion under conditions of superplasticity [8] . Due to the high diffusion rate in the deformation zone and the fine-grained structure of the samples, the extrusion of alloys ensures complete homogenization of the solid solution compared to other technological methods. In addition to the stoichiometric composition, alloys with partial replacement of Te by Se (up to 5 atm%) are of interest as effective materials for thermoelectric cooling along the cross-section x=0.5 for a certain p-type thermoelectric. studied.

Thermocouples produced by cold pressing, directional crystallization, and extrusion have some disparity in composition and properties along the length and cross-section of the ingots[9]. Due to heterogeneity, in connection with this method, Z_te is reduced by 10÷12%. Chokhralsky obtained single crystals of solid solutions based on bismuth and antimony chalcogenides, which are highly homogeneous and $Z = 3 \cdot 10^{-3}$ grad.

In the literature [10] there is information about methods of obtaining samples with high Z=(3.8÷4.0) $Z = 3 \cdot 10^{-3}$ град$^{-1}$. However, these results have not yet been replicated. Therefore, further development of experimental-industrial technology that allows to obtain highly efficient thermoelectric materials in successive batches ($Z = 3 \cdot 10^{-3}$) is a particularly important task.

For solid solutions with a narrow range $\mathrm{E_g}$ ($\mathrm{E_g} <$ 0,2 эВ), including solid solutions based on bismuth tellurium, the parameter $\left(\frac{\mathrm{m_n}}{\mathrm{m_0}}\right)^{\frac{3}{2}}\mathrm{U_0}$ ($\mathrm{m_n}$)is effective [11]. 'shown. mass density of states, $\mathrm{m_0}$ is the mass of a free electron, $\mathrm{U_0}$ is the mobility of charge carriers in the absence of degeneracy of the electron gas, and the thermal conductivity of the crystal lattice, which determines the thermoelectric index, χ_p. the quality of materials can change significantly under the influence of internal conductivity at 300 K.

$Bi_2Te_{3-x}Se_x$ $(x = 0,12 \div 0,16)$was brought to stoichiometric composition by adding excess stoichiometric tellurium to the charge according to the comparative study of electrical conductivity of alloys. and the same alloys that deviate from tellurium stoichiometry. under experimental conditions, the amount of over stoichiometric tellurium added to the charge and required to compensate for bismuth against the structure when crystals are obtained by the Bridgman method is 0.25 and 0.5 wt %, respectively. $\mathrm{Bi_2Te_{2,4}Se_{0,6}}$ alloys $\mathrm{Bi_2Te_{2,88}Se_{0,12}}$and p-type are presented. Solid solution based on Bi_2Se_3 5 mol% $\underline{Sb_{1,5},\mathrm{Bi}_{0,5}\mathrm{Te}_3\ Z_m = 3 \div 3{,}1 \cdot 10^{-3}\frac{1}{\mathrm{K}}(T = 300\ K)}$ It is characterized by K (T=300 K). It is achieved by a significant reduction of χ_p.

In the literature, there is information that Bi_2Te_3 solid solutions with chalcogenides of some rare earth elements have interesting thermoelectric properties [14-I6], state diagrams of a large number of Bi_2Te_3systems the results of the study are presented.

Results

The coefficient of thermal expansion of low-temperature materials was measured in the temperature range of 20÷400°C depending on their detailed composition. The table shows the value of these parameters at 20 ° C ÷ 400 ° C

Mechanical properties of low temperature materials

Table 1

Material	T ^{0}C	$\sigma_{изг}$ kg/mm^2	$\sigma_{сж}$ kg/mm^2	τ_c kg/mm^2	ε %	KTR 10^{-6} grad^{-1}
$(Bi,Sb)_2Te_3$	20	1,4	0,6	2,7	0,27	17,1
	400	0,1	0,7	0,6	3,69	
$(Bi,Sb)_2Te_3$	20	4,8	8,2	1,2	0,08	
	400	0,8	0,9	0,4	1,36	19,2
$Bi_2(Te,Se)_3$	20	2,0	7,8	2,8	0,36	16,5
	400	0,1	2,0	0,9	4,32	
$Bi_2(Te,Se)_3$	20	5,3	8,6	1,5	0,09	18,0
	400	0,8	2,3	0,5	2,20	

Various tests of the mechanical properties of solid solution single crystals based on Bi_2Te_3 have shown that they are very sensitive to mechanical defects and local overstresses. Only two test schemes are accepted - bending and compression

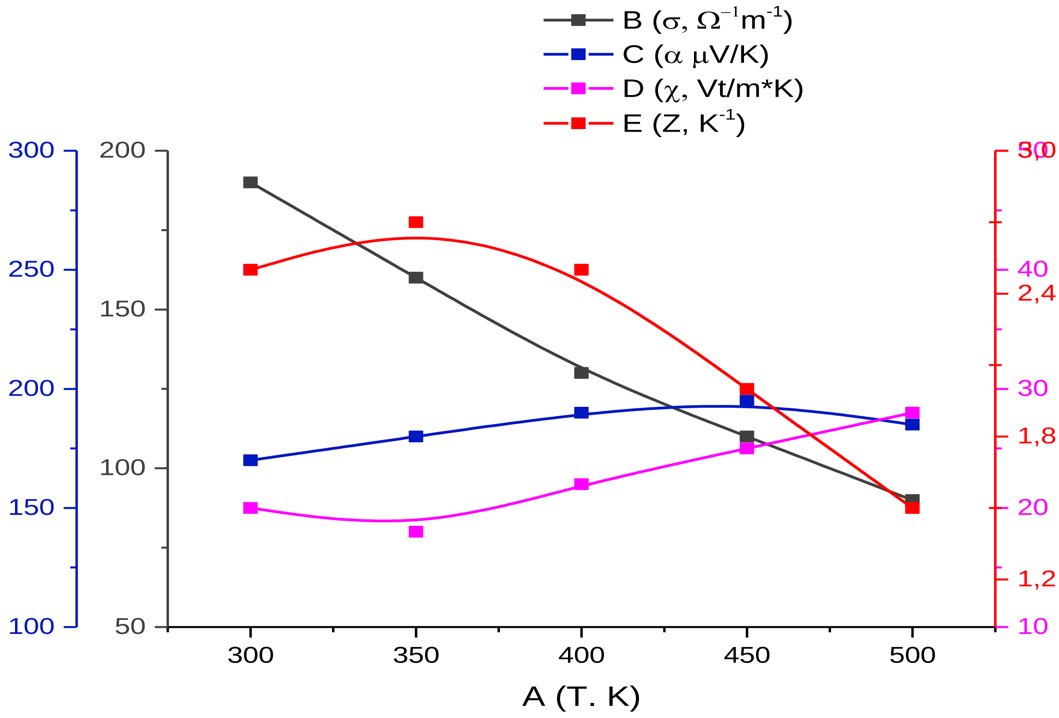
Single crystals are oriented by taking pictures in an RKV camera. Specimens were cut from single crystals by electric spark cutting for compression (2x3x6 mm^3) and bending (3x6x45mm^3) tests. The compression test was carried out with the load directions (1010) and (0001), the bending test was carried out on a special device with a three-point scheme when loading with the base perpendicular to the (0001) and (1210) planes. 24 mm, compression strain rate 0.05 cm/min bending 0.005 cm/min.

Before awarding, the sample was kept at a certain temperature for 30 minutes to achieve thermal equilibrium in the chamber, despite all the precautions, the spread of the data was very important. From what has been said, it is clear that when planning the composition of strength, not the average, but the maximum values achieved are an indicator, and lower values due to defects should be taken into account.

The results of the study of the influence of the composition and state of $Bi_2\mathrm{Te}_3 - Bi_2Se_3$ solutions on the deformation mechanism, as well as on the mechanical properties of materials and their temperature dependence are highlighted.

The mechanical properties of $\mathrm{Bi_2Te_3}$, $\mathrm{Bi_2Te_{2,88}Se_3}$ and $\mathrm{Bi_2Te_{2,4}Se_{0,6}}$were studied.

The stress-strain curves obtained at all temperatures for the solid solution $\mathrm{Bi_2Te_{0,88}Se_{0,12}}$ have two distinct stages of deformation. The first stage is characterized by the linear dependence of the stress on the strain, the second is related to the non-linear nature of the dependence and ends with the destruction of the sample.



Picture 1. $Bi_{0,5}Sb_{1,5}Te_3$ Composition of thermoelectric parameters of the semi-element on temperature.

Despite many studies of solid solutions based on Bi and Sb chalcogenides and progress in the development of thermal converters based on them, it should be noted that existing semiconductor materials are characterized by brittleness and low mechanical strength. This is one of the reasons why thermopiles have a high rejection rate. Therefore, the further search for new, more effective and strengthened compounds is very urgent. Based on the above information, the following was determined.

Compared with known compositions, 3-component alloys with n- $Bi_2Te_{2.4}$ $Se_{0.6}$, n-$Bi_2Te_{2.9}Se_{0.1}$ and -$Bi_2Te_{0,25}.Se_{0,75}$, $Bi_{0,5}Sb_{1,5}Te_3$ are promising for further research.

While maintaining a high level of thermoelectric properties, increasing the mechanical strength of the thermocouple allows reducing the percentage of rejections in the production of thermopiles.

Conclusion

A device for measuring basic parameters such as relative electrical conductivity σ ($Om^{-1}\cdot sm^{-1}$), thermal conductivity α (*mkV/K*), thermal conductivity χ (*J/m·s·K*), was collected and with its help, the thermoelectricity of the obtained material was evaluated.

As a result of the study of the thermoelectric properties of the Bi_2Te_3-Bi_2Se_3 alloy depending on the lead concentration, the main parameters of the material $\sigma = 1500\ Ом^{-1}см^{-1}$, α=175 mkV/K are optimal values are 0.05 mass per frost. Fixed to occur when % lead is inserted.

Based on theoretical calculations, it is shown that when using a thermocouple with extended networks, it is preferable to use the combined operating mode of non-stationary thermoelectric cooling, in which more effective cooling is achieved at the same value of thermoelectric efficiency, that is, the overall temperature drop increases.

References

1. Onarkulov K., Azimov T. Diffusion processes in contact areas thermoelements based on Pb-Sb alloys //American Institute of Physics Conference Series. – 2024. – T. 3045. – №. 1. – C. 030096.
2. Onarkulov, K. E., & Azimov, T. M. (2023). Study of diffusion processes in contact areas of

thermocouples with metals. *International Journal of Physical Sciences*, *18*(1), 59-64.

3. Azimov, T. M., Gaynazarova, K. I., Onarkulov, M. K., & Yuldashev, A. A. (2021). Thermoelectric and Galvanomagnetic Properties of the Alloy Bi_2Te_3+ 0.04 Weight% Ni in the Temperature Range 77÷ 300 K. *American Journal of Modern Physics*, *10*(6), 124-128.
4. Karimberdi, O., Usmanov, Y., & Toolanboy, A. (2020). Semiconductor sensor for detecting volume changes at low temperatures. *European Journal of Molecular & Clinical Medicine*, *7*(2), 2353-2358.
5. Onarkulov, K. E., Yuldashev, A. A., Azimov, T., & Yo'ldoshqori, SH. (2017). Vismut-surma tellurid yupqa pardalarning elektrofizik xossalariga texnologik jarayonning ta'siri. *FarDU ilmiy xabarlar*, *2*, 32-35.
6. Azimov, T., Gajnazarova, K., & Onarkulov, K. (2020). Method for determining the contact resistance of thermoelements. *Euroasian Journal of Semiconductors Science and Engineering*, *2*(5), 11.
7. Daliev, K. S., Azimov, T. M. R., & Onarkulov, M. K. (2020). Influence of doping impurities on mechanical and thermoelectric properties of cooling themoels based on bismuth and antimony chalcogenides. *Euroasian Journal of Semiconductors Science and Engineering*, *2*(1), 1.
8. Azimov, T. M. (2022). Elektrofizicheskiye svoystva poluprovodnikovix soyedineniy *Journal of new century innovations*, *19*(1), 95-98.
9. Onarkulov, K. E., Azimov, T. M., & Onarkulov, M. K. (2020). Issledovaniye diffuzionnix protsessov, proxodyashix v prikontaktnoy oblasti v oxlajdayushix termoelementax iz Bi_2Te_3 v Sb_2Te_3. *Yangi materiallar va geliotexnologiyalar*, 46.
10. M.Z. Xayitoxunova, D.I.A'zamova, & T.M.Azimov. (2023). Bi_2Te_3 asosida olingan termoelektrik elementlarning elektrofizik parametrlari. *Fergana State University Conference*, 251–254. Retrieved from