World Journal of Applied Physics
2023; 8(1): 1-5
http://www.sciencepublishinggroup.com/j/wjap
doi: 10.11648/j.wjap.20230801.11
ISSN: 2637-5990 (Print); ISSN: 2637-6008 (Online)

Effect of Annealing on Thermoelectric Properties of Crystals $Yb_xBi_{2-x}Te_3$

Famil Imran Mamedov[1], Seyyara Adil Nabieva[1, 2], Sevinj Zellabdin Melikova[1, 3], Gunel Talat Imanova[3, *]

[1]Academy of the Ministry of Emergency Situations of Azerbaijan, Baku, Azerbaijan

[2]Institute of Physics, Minister of Science and Education Republic of Azerbaijan, Baku, Azerbaijan

[3]Institute of Radiation Problems, Minister of Science and Education Republic of Azerbaijan, Baku, Azerbaijan

Email address:

gunel_imanova55@mail.ru (Gunel Talat Imanova)

[*]Corresponding author

To cite this article:

Famil Imran Mamedov, Seyyara Adil Nabieva, Sevinj Zellabdin Melikova, Gunel Talat Imanova. Effect of Annealing on Thermoelectric Properties of Crystals $Yb_xBi_{2-x}Te_3$. *World Journal of Applied Physics*. Vol. 8, No. 1, 2023, pp. 1-5. doi: 10.11648/j.wjap.20230801.11

Received: December 2, 2022; **Accepted**: December 21, 2022; **Published**: March 4, 2023

Abstract: The work is devoted to the study of the thermoelectric properties of solid crystal $Yb_xBi_{2-x}Te_3$. In the work presents the results of studies of the thermoelectric properties of $Yb_xBi_{2-x}Te_3$ ($x\leq0.10$) solid solutions before and after annealing in the temperature range (300-580)K. Regularities of changes in the electrical conductivity, Seebeck coefficient and total thermal conductivity of the samples depending on the content of ytterbium (Yb) are established. Dependences of electrical conductivity, Seebeck coefficient, thermal conductivity on temperature for the crystal under study are plotted. Temperature curves were recorded using a Termoscan-2 low-frequency temperature recorder at a heating rate of 283 K/ min. Temperature measurements of phase transformations were carried out with combined chromel-alumel thermocouples. Studies of conductivity σ, thermoelectric power (S). were carried out by the four-probe method at direct current in the temperature range of 300-600 K. Ohmic contacts were applied using alloys. It has been established that the optimal combination of these thermoelectric characteristics is achieved for the compositions x = 0.1, which are characterized by the maximum thermoelectric index (ZT=0.87) of the figure of merit in the temperature range of 420-500 K after annealing at 500 K for τ=240 hours. It was revealed that the $Yb_xBi_{2-x}Te_3$ systems under study are n-type semiconductor thermoelectric materials in the temperature range of 300-600K.

Keywords: $Yb_xBi_{2-x}Te_3$, Thermoelectric, SEE Beck Coefficient, Conductivity, Efficiency

1. Introduction

Recently, the possibility of increasing the thermoelectric efficiency of various thermoelectric materials, including Bi_4Te_3, through the use of various dopant impurity additives, has been widely studied [1-4]. Doping of Bi_4Te_3 with lactanoids can affect the transport properties of thermoelectric materials by the following mechanism: 1) an increase in the density of states near the Fermi level; 2) the formation of local defects leading to additional scattering of charge carriers as a result of which the total thermal conductivity decreases [5-7]. As is known, the thermoelectric figure of merit of the used thermoelectric material, which can be expressed as $ZT=S^2\sigma/\chi T$ or $(S^2/\rho\chi)T$, where S, σ and χ - Seebeck coefficient, specific conductivity or resistivity and total thermal conductivity of materials, respectively, T - absolute temperature. It is obvious that an effective thermoelectric material must simultaneously have a large value S and a low value ρ and χ (or large value σ). There is a huge number of materials in which the combination of S, ρ and χ turns out to be acceptable for their practical application as thermoelectric materials. At present, solid solutions of composition $Bi_2Te_{2,7}Se_{0,3}$ possessing an electronic type of conductivity are one of such materials for low-temperature thermoelectric applications. However, the thermoelectric figure of merit of these solid solutions is not very high (ZT≈1), which significantly limits the potential for their widespread use [8-11]. Therefore, the search for scientific and technological ways to increase the thermoelectric figure of merit of $Bi_2Te_{2,7}Se_{0,3}$ compounds is an urgent task.

Controlling with various impurities often turns out to be a fairly effective way to optimize the main thermoelectric characteristics, which promotes an increase in Bi_2Te_3 based compounds [10-12]. Recently, it was found that rare earth elements are one of the most effective impurities in the structure of Bi_2Te_3 [4-13]. In contrast to Bi_2Te_3, the effect of alloying with various rare-earth elements on the thermoelectric properties of solid solutions of Bi_2Te_3 has been studied much less, which stimulated research, the results of which are presented in the article [14, 15].

In this work, the main attention is paid to the effect on the parameters Bi_2Te_3 depending on the content of the ytterbium (Yb) impurity and the effect of annealing on the parameters characterizing the thermoelectric efficiency of solid solutions $Yb_xBi_{2-x}Te_3$ (x≤0,10) [16].

2. Experimental Technique

The synthesis of alloys of solid solutions $Yb_xBi_{2-x}Te_3$ was carried out by fusing high-purity elementary components in quartz ampoules evacuated to 1.33 Pa at a temperature of 1175-1273 K. Bismuth grade 99,99%, ytterbium (Yb) - 99.98, tellurium grade Te – 98,98% were used as initial elementary substances. To homogenize the alloys, annealing was carried out at 800 K for 48 h. The alloys of solid solutions $Yb_xBi_{2-x}Te_3$ were studied by DTA, X-ray phase (XRD), microstructural (MSA) analyzes, as well as measurements of microhardness and determination of density. Temperature curves were recorded using a Termoscan-2 low-frequency temperature recorder at a heating rate of 283 K / min. Temperature measurements of phase transformations were carried out with combined chromel-alumel thermocouples. Heating and cooling of alloys was carried out in electric resistance tube furnaces Al_2O_3. X-ray powder diffraction patterns were recorded on a diffractometer D2PHAZER (CuKa – irradiation). The MSA of the system alloys was investigated using a MIM-8 metallographic microscope on pre-etched thin sections with a paste. When studying the microstructure of the alloys, etchant of composition HNO_3:H_2O_2=1:1 was used. The etching time was 20 s.

The microhardness of the alloys of the system was measured on a PMT-3 microhardness tester at loads of 0.10 and 0.20 N. The density of the alloys of the system was determined by the pycnometric method; toluene was used as a working fluid.

The single crystallinity of the samples was confirmed by X-ray diffraction analysis. the samples were of size 3x6x18 mm^3. Studies of conductivity σ, thermoelectric power (S). were carried out by the four-probe method at direct current in the temperature range of 300-600 K. Ohmic contacts were applied using alloys. The content of Yb varied from x = 0.000 to 0.100.

3. Results and Discussion

Samples of solid solutions $Yb_xBi_{2-x}Te_3$ were obtained in the form of compact dark gray ingots. The alloys are resistant to air and water. Concentrated mineral acids (HCl, HNO_3) decompose them, while organic solvents do not act on them.

Bridgman-Stockbarger methods grown single crystals of solid solutions $Yb_xBi_{2-x}Te_3$ (x=0,000; 0,010; 0,015; 0,020 and 0,100). Obtaining single crystals with the parameters necessary for practical application is a difficult scientific and technical problem. To date, the use of the Bridgman method, implemented in multi-zone thermal installations, shows good results for many technically complex substances. One of the main requirements put forward by the technological process of growing crystals for thermal equipment is the stability of maintaining the temperature field in the working volume of the installation. Changes in the temperature field cause deviations in the growth rate of the crystal from the nominal speed of movement of the growth container, which can negatively affect the perfection of the growing crystal.

The temperature dependences of the investigated thermoelectric parameters (S, σ and χ) before annealing are shown in Figures 1-3.

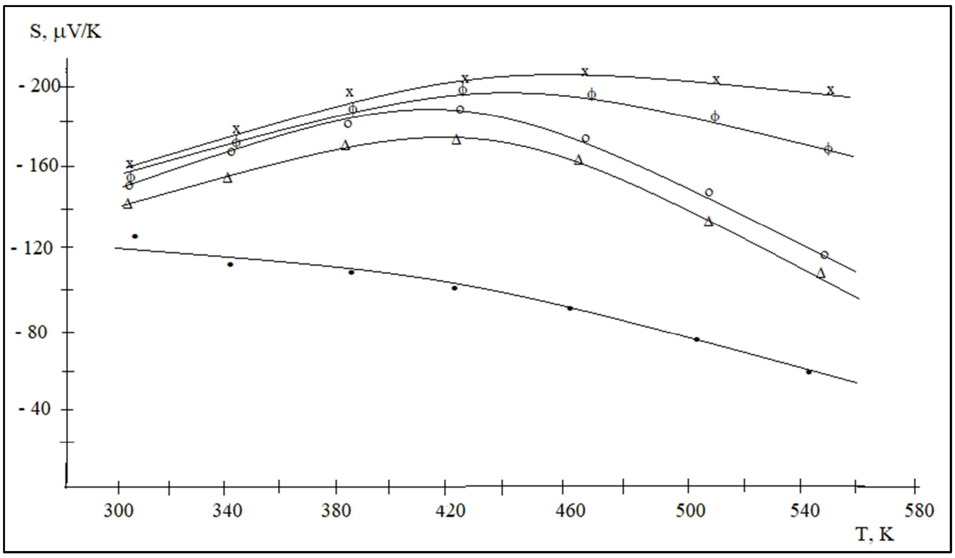

Figure 1. *The dependence of the Seebeck coefficient on temperature in $Yb_xBi_{2-x}Te_3$.*

Figure 1 shows the temperature dependences of the Seebeck coefficients of the samples under study in the temperature range of 300-580K.

Note that the work considered two main issues: 1) the effect of impurity Yb on the thermoelectric properties of Bi_2Te_3, i.e. how does it affect the parameters when substituting bismuth for ytterbium. 2) the effect of annealing on the thermoelectric parameter of the studied compositions of the samples. It can be seen from Figure 1 that when bismuth is replaced by ytterbium, the Seebeck effect increases in the investigated temperature range of 300-580K. Regardless of the Yb content, the Seebeck coefficient relatively increases with increasing temperature up to T≤ 450K. T >450K, the S(T) values of sample No. 1 and 2 decreases monotonically to S≈-100μV/K; and samples 3 and 4, where the ytterbium content is greater than S(T), varies in different ways and the S(T) dependence is slowly decreasing.

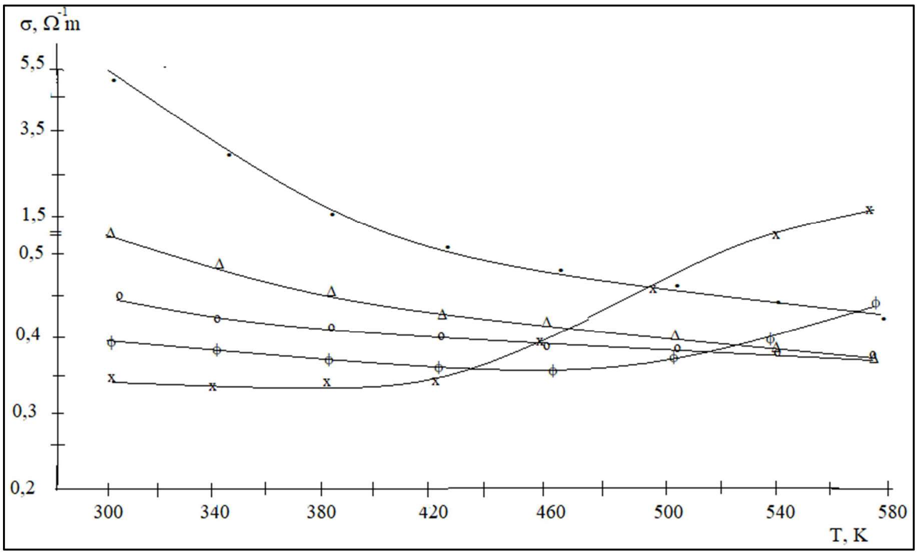

Figure 2. *The dependence of the electrical conductivity on temperature in* $Yb_xBi_{2-x}Te_3$.

Figure 2 shows the temperature dependences of the electrical conductivity of the samples under study. It can be seen from the figures that, depending on the ytterbium content in the alloy, the values of T change in different ways. In the temperature range 300-400K σ(T) decreases, while σ(T) decreases with increasing concentration of ytterbium. In addition to sample No. 1, the rest in the composition, the value of σ increases with increasing temperature.

Analyzing the results, it can be concluded that, depending on the content of the ytterbium impurity in solid solutions, additional scattering centers appear due to bipolar diffusion, and S(T) above 440K decreases, and σ(T) increases markedly.

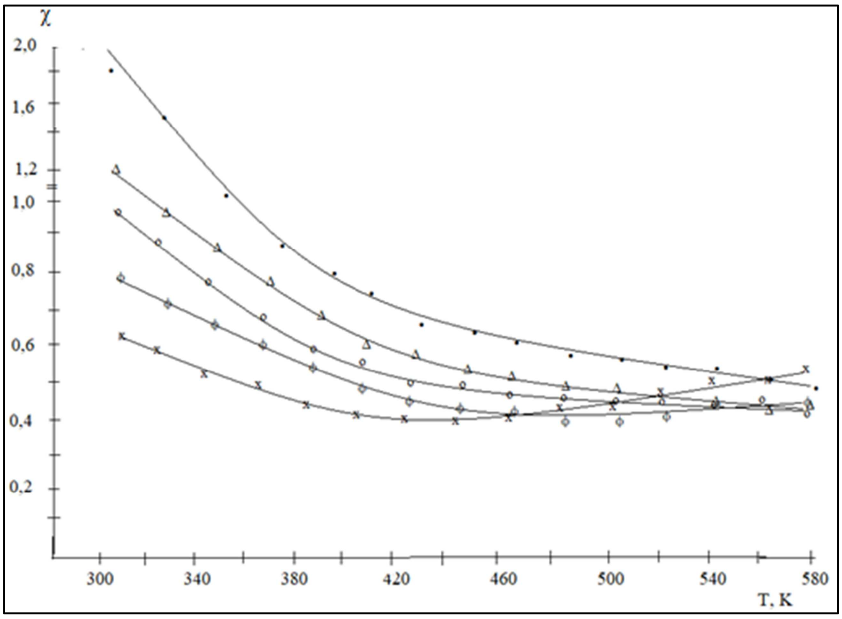

Figure 3. *The dependence of the thermal conductivity on temperature in* $Yb_xBi_{2-x}Te_3$.

Figure 3 shows the temperature dependences of the total thermal conductivity (χ(T)) of the samples under study (before heat treatment). As can be seen from Figure 3, with increasing T, the value of χ(T) decreases. At the same time, in the samples under study, with an increase in the Yb impurity content, the χ(T) value decreases. From Figure 3 it can be seen that in samples 3 and 4, starting at T ≥480K, the value of χ(T) increases, which directly confirms (corresponds) to the regularity of T.

The following instruments were used to measure the kinetic parameters: voltmeters V7-21, V.7.21A; power supply B5-49, TES-41, Shch4313; potentiometer P4833; ammeters M231; M253, as well as resistance store MP-63; P33.

The measurements were carried out in an absolutely stationary mode in an evacuated (P = 0.1 Pa) cryostat. The temperature gradient along the sample was: ΔT = 6-9°C. The error of changes (σ, S and R_x) did not exceed 2.7%. with changes in χ, the error was 6.2%.

As you know, annealing the material makes it possible to improve the uniformity of the resistivity and its behavior during operation. Basically, the uniformity of resistivity is also determined by the uniformity of doping in which it strongly affects the kinetic parameters of the sample, especially the compositions with defect structures of the crystal lattice. Taking into account all this, the above indicated compositions of the samples obtained by us are given by annealing at different temperatures (T = 400 and 520 K) for t = 240 hours. After annealing, the same kinetic parameters (σ, S and χ) were measured each time and the results obtained are shown in Table 1.

Table 1. *Thermoelectric parameters: σ(Om.m): 10^{-6}S(V/K); 10^{-3}χ(Vt/m.K); 10^{-3}Z(T).*

σ	S	χ	Z	σ	S	χ	Z	σ	S	χ	Z
Before annealing											
5.6	-120	1.9		4.1	-105	0.8		3.3	-75	0.5	
5.2	-140	1.2		2.9	-170	0.6		2.4	-120	0.4	
4.2	-151	1.0		2.5	-175	0.5		2.4	-135	0.4	
4.1	-154	0.7	1.2	2.3	--182	0.4	1	2.6	-165	0.3	2
3.7	-160	0.6	1.5	2.5	-200	0.4	2	4.0	-190	0.6	2
After annealing at 400K t=240 hours											
5.3	-132	1.8		3.8	-135	1.8		3.0	-125	0.6	
5.1	-145	1.1		3.7	-145	1.0		3.6	-130	0.5	1
4.0	-160	1.0	1.3	3.6	-165	1.0	1	3.5	-155	0.4	1
4.1	-160	0.8	1.7	3.9	-172	0.7	2	3.8	-168	0.7	1
3.8	-175	0.6		3.7	-188	0.6		4.2	-190	0.6	2
After annealing at 500K t=240 hours											
5.1	-160	2.0	1	4.5	-165	0.9	1	3.0	-130	0.7	1
4.9	-180	1.8	1	4.6	-192	0.7	2	3.9	-158	0.5	1
4.5	-190	1.6	1	4.6	-205	0.6	2	3.8	-175	0.6	1
4.2	-195	1.1	1	4.5	-208	0.6	3	3.8	-218	0.6	2
4.6	-205	1.4	2	4.7	-240	0.8	3	3.6	-220	0.5	3

As can be seen from the table, annealing at 400 and 520 K for 240 hours significantly changes the value of the thermoelectric parameters of the samples with ytterbium impurities in comparison with the annealed samples. After annealing, the thermoelectric efficiency of the material is significantly improved. Annealing the samples does not change the type of conductivity, and all compositions remain n-type. As can be seen from the table, a particular change in parameters (σ, S and χ) in samples No. 5 is manifested at T = 400K, since in the annealed samples the value of these parameters increases:

$$\frac{\sigma_{400}}{\sigma_{\frac{n}{ann}}} = \frac{375-250}{250} = 50\%$$

$$\frac{\chi_{400}}{\chi_{n/ann}} \approx 39{,}5\%$$

At 520K σ≈4,3%, after annealing at 500K these parameters are: at 300K σ increases 24,3%; S-28,1%; χ-1,02%, At 420K σ-88%; S-20%; χ-90,7%,

As can be seen from the table, in samples annealed at 500K No. 4 and 5, the figure of merit (thermoelectric) changes η=1,38-1,67 in the temperature range T = 400-520K and, as can be seen, the thermoelectric figure of merit in these compositions (sample 5) is much higher ($Z=3{,}3\cdot10^{-3}K^{-1}$). The same results are obtained in annealed samples No. 5 at 500K and 520K. Analyzing the obtained data from the table shows that samples No. 4 and 5 from solid solutions $Yb_xBi_{2-x}Te_3$ are promising thermoelectric materials for thermogenerators: 1,38<η≤1,67.

Determination of the mechanisms of the influence of doping with ytterbium on these properties, as well as the identification of the exact compositions for practical use, will be the subjects of further research.

4. Conclusion

It was revealed that the investigated systems $Yb_xBi_{2-x}Te_3$ are n-type semiconductor thermoelectric materials in the temperature range of 300-600K. Experimental results show that after annealing at 500 K for t = 240 hours, the kinetic parameters are significantly improved relative to the unannealed composition. The most effective are those containing ytterbium x = 0.02 and 0.10 in which $Z=3{,}3\cdot10^{-3}K^{-1}$; η=1,15-1,67.

References

[1] A. V. Dmitriev, I. P. Zvyagin. "Modern trends in the development of the physics of thermoelectric materials", UFN, vol. 180, no. 8 (2010).

[2] A. V. Shevelkov. "Chemical aspects of creating thermoelectric materials", Uspekhi khimii, 77 (1) (2008) pp. 3-21.

[3] Xiaolei SHI, Xin AI, Qihao ZHANG, Xiaofang LU, Shijia GU, Li SU, Lianjun WANG, WanJANG "Enhanced thermoelectric properties of hydrothermally synthesized SeLu-codoped Bi_2Te_3@ Journal of advanced Ceramics (2020), 9 (4), 424-431.

[4] A. U. Vasiliev, M. N. Yapryntsev, O. N. Ivanov, M. V. Zhezhu. "Thermoelectric properties of solid solutions $Bi_{2-x}Lu_xTe_{2,7}Se_{0,3}$" FTP (2019) volume 53, v. 5, p. 680-684.

[5] M. N. Yapryntsev, R. A. Lyubushkin, O. N. Soklakova, O. N. Ivanov. "Synthesis and electrophysical properties of a thermodynamic material based on Bi_2Te_3, doped with lanthanides Er, Tm, Yb and Lu", FTP (2017), volume 51, v. 6, pp. 744-747.

[6] L. P. Bulat, A. I. Drobkin, V. V. Karatayev, V. B. Osvensky, D. A. Pshenai-Severin FTT, 52 (9), 1712 (2010).

[7] J. Yang, F. Wu, Z. Zhu, J. Yao, H. Song, X. Hu. J. Alloys Comp. 619, 401 (2015).

[8] O. Ivanov, M. Yaprintsev, R. Lyubushkin, O. Soklakova. Scr. Mater, 146. 91 (2018).

[9] Y. Pan, TK. Wer, C. F. Wu, JF Li. J. Mater. Chem., Cj. 10583 (2015).

[10] A. Vasilev, M. Yaprintsev, O. Ivanov, E. Danshina. Sol. St. Sci., 84, 28 (2018).

[11] F. Wu, H. Z. Song, F. Gao, W. Y. Shi, J. F. Jia and X. Hu. J. Electronic. Mater. 42.1140 (2013).

[12] Snyder GJ., Toberer E. S. Complex thermoelectric materials. Nat. Mater. 2008, 7. 105-114.

[13] Fang T., Li X., Hu CL et al. Complex band structures and lattice dynamics of Bi_2Te_3-based compounds and Solid solutions. Adv. Func. Mater (2019). 29.

[14] Ji XH, Zhao XB, Zhang YH, et al. Synthesis and properties of rare earth containing Bi_2Te_3 based thermoelectric alloys. J. Alloys Comp. (2005) 387. 282-286.

[15] Wu F. Song HZ Jia JF, et al. Effects of Ce Y and Sm doping on the thermoelectric properties of Bi_2Te_3 alloy. Prog. Nat. sci. mater. Int. (2013) 23. 408-412.

[16] Cao RJ, Song HZ, Cao WX et al. Thermoelectric properties of Lu –doped n-type $LuBi_{2-x}Te_{2,7}Se_{0,3}$ alloys. J. Alloys Compd 92017), 727. 326-331.