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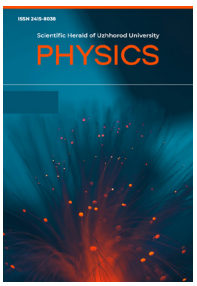

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Thermal conductivity of solid solutions of $Bi_2(Te_{1-x}Se_x)_3$ (x = 0-0.07)

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Abstract

Relevance. Solid solutions $Bi_2(Te_{1-x}Se_x)_3$ are effective materials for an *n*-leg of thermoelectric cooling devices. Recently, concentration anomalies of properties with a low impurity content were detected in these solid solutions (x ~0.01). It is important to establish whether similar anomalies would be observed on the dependence of thermal conductivity λ from the composition of the solid solution, since λ is one of the parameters that determine the thermoelectric quality factor of the material.

Purpose. The purpose of this study was to investigate the concentration dependences of the thermal conductivity of the solid solution of $Bi_2(Te_{1-x}Se_x)_3$ in the interval x = (0-0.07) to identify concentration anomalies and their possible impact on thermoelectric (TE) efficiency.

Methodology. Investigation of temperature dependences of thermal conductivity λ was performed by a dynamic calorimeter. Isotherms of λ for different temperatures in the range T = 175-400 K were built on their basis.

Results. On isotherms of λ, there is an interval of abnormal growth λ, which becomes more pronounced when the temperature decreases. The presence of this interval is associated with critical phenomena that accompany the transition of the percolation type from dilute to concentrated solid solutions.

Conclusions. The estimation of the thermoelectric figure of merit Z of materials is given. It is shown that the detected growth of λ leads to a decrease in Z in the ranges near the critical (x = 0.01), which should be considered in the practical use of solid solutions of $Bi_2(Te_{1-x}Se_x)_3$

Keywords: thermoelectric materials V_2VI_3, thermal properties, composition, percolation, thermoelectric figure of merit

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Introduction

It is known [1-3] that the efficiency of a thermoelectric (TE) material is largely determined by the value of its TE figure of merit ($Z=S^2\sigma/\lambda$, where S – Seebeck coefficient, σ – electrical conductivity, λ – thermal conductivity of the material). The most important task of materials science is to find ways to improve Z, including by a decrease in thermal conductivity [4; 5]. One of the conventional ways to increase Z, proposed in 1956 [6] – creation of solid solutions (SS) based on promising thermoelectrics.

Semiconductor alloys $Bi_2(Te_{1-x}Se_x)_3$ in the field of existence of solid solutions (x~0-0.2 and x~0.5-1, respectively [7; 8]), are known as effective materials for n-legs of TE cooling devices operating at temperatures near room temperature [1; 2; 9]. The maximum Z in these SS was obtained in the range of compositions x=0.07-0.2 (exact interval x depended on the technology of samples' manufacturing) [10-12].

Earlier in the study of concentration dependencies S and σ cast and cold-pressed samples of the system $Bi_2(Te_{1-x}Se_x)_3$, the authors of this study observed anomalies of properties near the composition x = 0.01, the presence of which was associated with the phase transition (PT) from diluted to concentrated solid solution [13]. Similar anomalies were observed earlier in [14] for a large number of solid solutions. Additional evidence in favour of this assumption was the discovery in [15] of a peak on the concentration dependence of heat capacity C. If such a PT occurs, it would certainly also affect the concentration dependence of λ, and, accordingly, the nature of the Z(x) dependence.

Thermal conductivity of solid solution of $Bi_2(Te_{1-x}Se_x)_3$ has been widely studied to date. Temperature dependencies λ of $Bi_2(Te_{1-x}Se_x)_3$ SS are given in a number of studies [16-18]. For SS of $Bi_2(Te_{1-x}Se_x)_3$ there are three components of thermal conductivity that influence the course of dependence λ(T): electronic, lattice, and bipolar thermal conductivity. The ratio of λ components of the material depends on the manufacturing technology, and on the heat and mechanical treatment of the sample. The transition to bipolar heat transfer with increasing temperature should be accompanied by an increase in λ. Currently, available data on the bipolar component of λ are somewhat contradictory. Thus, growth of λ at temperatures above T = 350 K was observed in pure Bi_2Te_3 in [16], and in SS of $Bi_2(Te_{1-x}Se_x)_3$ in monocrystalline samples in [18]. However, in the studies [17; 19] in composite samples of SS $Bi_2(Te_{1-x}Se_x)_3$ (x = 0-1) growth of λ was not observed.

Many studies have data of the dependence of λ on the composition of SS of $Bi_2(Te_{1-x}Se_x)_3$ x for monocrystalline [20; 21] and polycrystalline [19; 22] samples. According to this data, the dependency λ on the composition of the SS is a curve with two minima, between which there is a local maximum at x~0.33 [9]. In [20], it was shown that this composition of SS corresponds to the establishment of an ordered compound Bi_2Te_2Se.

To date, for $Bi_2(Te_{1-x}Se_x)_3$ SS there are no detailed studies of concentration dependence λ in the composition interval near pure Bi_2Te_3.The question arises: will the concentration dependencies of thermal conductivity reproduce the anomalies that the authors observed on the concentration dependencies σ and S in previous studies [13; 15]. The study of λ for small samples samples with small values of x would allow estimating the value of Z and drawing a conclusion about the influence of property anomalies on the TE figure of merit of SS of $Bi_2(Te_{1-x}Se_x)_3$.

The purpose of this study was to investigate the concentration dependences of the thermal conductivity of SS of $Bi_2(Te_{1-x}Se_x)_3$ in the interval x = (0-0.07) to identify concentration anomalies and their possible impact on thermoelectric efficiency.

Materials and Methods

Cold-pressed tablets (diameter d = 15 mm and height h = 5 mm) of $Bi_2(Te_{1-x}Se_x)_3$ ($0 \le x \le 0.07$) for measuring λ were made from annealed ingots of the solid solution of $Bi_2(Te_{1-x}Se_x)_3$ SS. For the production of ingots, a mixture of high-purity (99.999% of the main element) Bi, Se, and Te with the corresponding ratio of components was placed in quartz ampoules pumped to a pressure of ~10^{-3} Pa. The ampoules were heated in a furnace to ~1,200 K and kept at this temperature for 5-6 hours using vibration mixing. The samples were then annealed for 200 hours at 820 K, and then cooled to room temperature. The resulting ingots were ground into powder in an automated SBMM agate mortar. The resulting powder was sifted through a sieve (cell size 200 microns). The powder was pressed at room temperature on a hydraulic press (pressure P = 7 t/cm^2, exposure time under load – 1 min.). After manufacturing, the tablets were annealed in evacuated ampoules made of heat-resistant glass for 200 hours at a temperature of T = 575 K and cooled at the speed of the switched-off furnace.

Thermal conductivity measurements were performed on a dynamic calorimeter IT-λ-400 in the temperature range of 175 K – 625 K. Before installing the sample into the experimental cell, the contact surfaces were sanded to a mirror-like gloss and a thin layer of KPT-8 thermal paste was applied to them. After the sample was installed, the experimental cell was cooled with liquid nitrogen to a temperature of ~150 K. The study was conducted in the monotonous heating mode at a speed of ~0.1 K/s. The thermal conductivity was measured in temperature increments of 25 K. To control the reproducibility of the results, the λ value for each sample was taken twice. When the sample was re-installed in the cell, a layer of thermal paste was re-applied to the contact surfaces. Thus,

the λ value for a sample of a certain composition, the data given in this paper represent the averaging of two measurements. Figure 1 shows the results of two measurements of λ for the sample Bi_2Te_3 (points 1 and 2 correspond to separate experiments). It can be argued that the results of two experiments for the same sample actually coincide within the margin of error. The root-mean-square error did not exceed 5%.

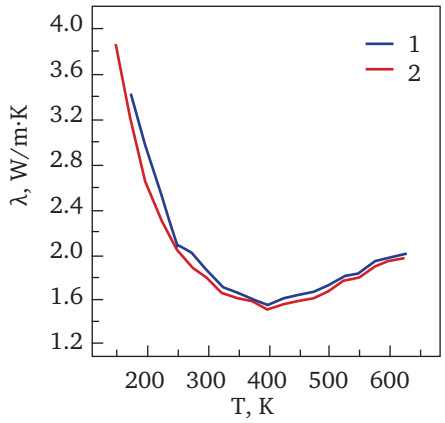

Figure 1. Experimental temperature dependences of thermal conductivity λ for a solution of Bi_2Te_3 (points 1 and 2 correspond to separate experiments)

Results and Discussion

Temperature dependences of thermal conductivity λ of cold-pressed and annealed SS of $Bi_2(Te_{1-x}Se_x)_3$ with different values of x are shown in Figure 2. You can see that for all samples λ first decreases in the temperature range T = 150 ÷ 350 K, after which at T=350÷625 K there is an increase in λ with increasing temperature. Such a course of dependence λ(T) indicates a change in the dominant heat transfer mechanism as the temperature increases.

Initial decline λ is associated with the fact that at temperatures below room temperature, heat transfer is provided by fluctuations in the crystal lattice (lattice thermal conductivity λ_L) and free electrons (electronic thermal conductivity λ_e). Both of these components decrease as the temperature increases, which leads to a decrease in the overall λ. Growth of λ at higher temperatures T~350 K can be explained by the fact that at these temperatures, the probability of heat transfer by electron-hole pairs increases (bipolar thermal conductivity λ_b) [16]. As noted above, such a course of temperature dependence of λ is typical for Bi_2Te_3 and SS on its basis, and was observed in [16; 18; 23]

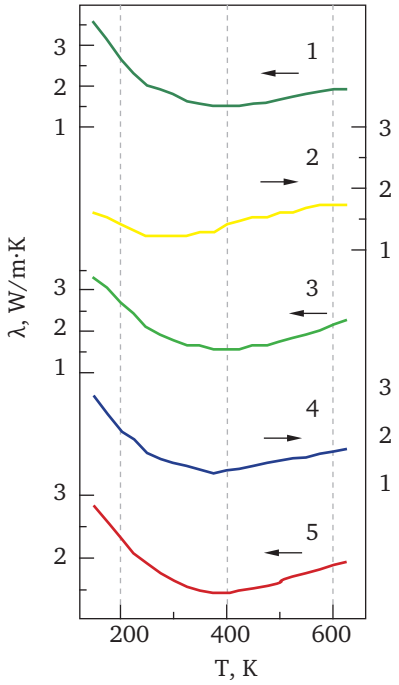

Figure 2. Temperature dependences of thermal conductivity λ for solid solutions of $Bi_2(Te_{1-x}Se_x)_3$ of different composition ($1 - x$ = 0; $2 - x$ = 0.005; $3 - x$ = 0.0125; $4 - x$ = 0.02; $5 - x$ = 0.045)

Based on temperature dependencies λ, thermal conductivity isotherms for temperature values T = 175; 225; 300; 350, and 400 K were constructed (Fig. 3). For all temperatures, a general downward trend towards a decrease in λ with increasing x can be observed, which corresponds to the available literature data [19-21]. It is known that the development of SS of Bi_2Te_3 and Bi_2Se_3 significantly reduces the lattice component of thermal conductivity compared to pure initial compounds and the ordered phase of Bi_2Te_2Se. Analysis of the data provided in various studies shows that the data on the dependence of $\lambda_L(x)$, are successfully described by the Calloway-von Bayer-Clemens model for scattering in SS [9].

It can be seen that for all temperatures after the initial decrease in λ, an interval of increasing thermal conductivity is observed (x = 0.005-0.01), resulting in a peak in the dependence λ (x). With increasing temperature, the magnitude (height) of the peak, which characterises the degree of growth in λ, decreases, and at 400 K the peak becomes hardly noticeable.

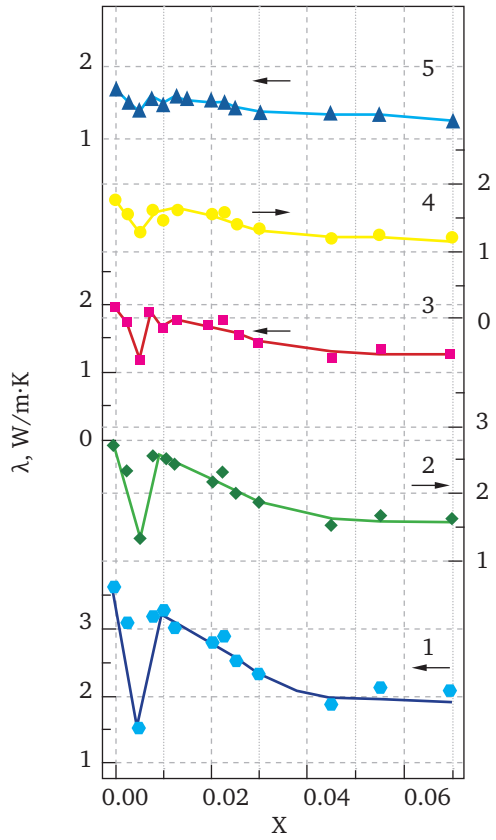

Figure 3. Thermal conductivity isotherms of λ of solid solutions of $Bi_2(Te_{1-x}Se_x)_3$ (*1* – T = 175 K; *2* – T = 225 K; *3* – T = 300 K; *4* – T = 350 K; *5* – T = 400 K)

Abnormal growth of λ in the interval x=0.005-0.01 is an additional evidence that in the specified range of compositions, transformations in the crystal are implemented during the formation of SS, which affect the processes of phonon scattering. As in previous studies [13], it is advisable to associate these transformations with the implementation of PT from diluted to concentrated solid solution. The likely mechanism for implementing these processes is described in detail in the review paper [14], which also provides a large number of experimental confirmations of this hypothesis. A more detailed description of these effects in relation to SS of $Bi_2(Te_{1-x}Se_x)_3$ is given in [13; 15].

These processes can be briefly described as follows. During isovalent substitution of Te→Se, a deformation sphere is formed around each impurity atom. Percolation theory, according to [24], states that there is a certain critical concentration of such spheres (the percolation threshold), at which they begin to interact collectively and a continuous chain of interactions (an infinite cluster) is created. Its development is a PT, the implementation of which results in anomalies in the dependencies of the properties of the SS on its composition. As in previous studies, the authors suggest calling solid solution diluted before reaching the threshold of percolation and the formation of an infinite cluster, and concentrated – after these processes have already passed.

Separately, it is worth noting that the growth of λ_L relative to neighbouring compounds at x = 0.033, which was observed in [19], may also be related to the proximity to a similar "percolation maximum" on dependency $\lambda_L(x)$.

In [13], the TE values of the parameters of cold-pressed and annealed samples $Bi_2(Te_{1-x}Se_x)_3$ were determined, namely, the electrical conductivity and Seebeck coefficient. Supplementing these data with the values of λ obtained in this study, the values of TE figure of merit Z for these SS at room temperature were calculated. The dependency Z(x) (Fig. 4a) also has a non-monotonic character: at the beginning of SS development, the figure of merit increases rapidly, reaching the value Z ~1.5 10^{-3} K^{-1} at x ~0.005. After that, in the interval x ~0.005-0.02 value Z decreases, after which there is an increase of Z up to x ~0.07.

Figure 4b shows the findings regarding dependency $Z(x)$ in comparison with the data of the studies [22] (hot-pressed samples) and [19] (composite samples). The Z values obtained in this study correspond to the data for samples made by other methods. The highest received value of Z corresponds to the composition x=0.07 and amounts to Z ~2.1 10^{-3} K^{-1} which within the error limit of the definition of Z coincides with the maximum value of Z, which was observed in [19] for composite materials.

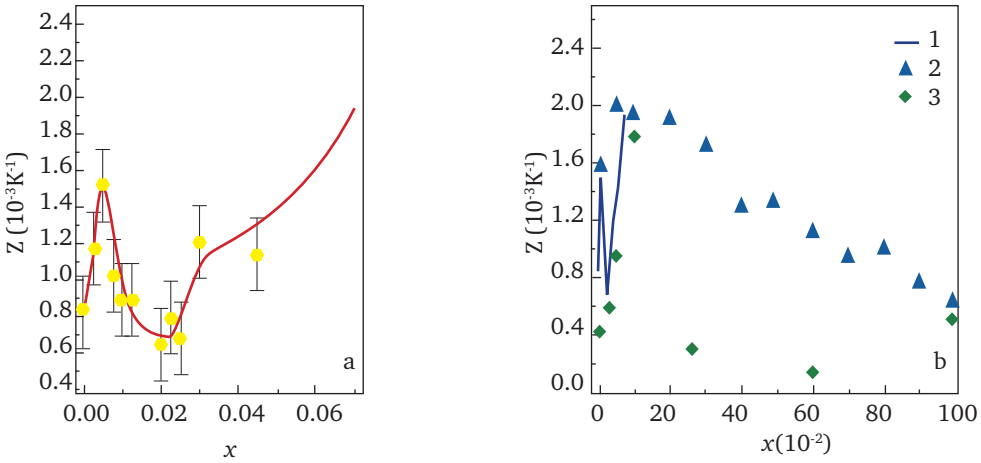

Figure 4. Dependence of thermoelectric figure of merit *Z,* which was calculated using the data from [13], on the composition of $Bi_2(Te_{1-x}Se_x)_3$ (x = 0-0.07) (a); Z(x) dependence obtained in this study, in comparison with the data of other researchers (*1* – this study, *2* –[22]; *3* – [19]) (b)

The results of this study, together with the results of [13], demonstrate that percolation PT affects all TE properties of SS of $Bi_2(Te_{1-x}Se_x)_3$, leading to an increase in electrical and thermal conductivity and a decrease in S in the area near x=0.01. But the effect of percolation PT on the TE figure of merit is determined by a combination of these parameters. In Figure 4b, the growth of λ in the proximity of percolation PT (x ~0.01) leads to a decrease in Z, compensating for growth σ, which was observed in [13] thus, SS has relatively high values of Z in the region befor PT (x = 0-0.005), and acquires maximum values in the region after PT (x ~ 0.07).

Conclusions

1. Temperature dependences (T = 175-600 K) of thermal conductivity λ of cold-pressed and annealed samples of solid solutions of $Bi_2(Te_{1-x}Se_x)_3$ in the interval of compositions (x = 0-0.07 are obtained and isotherms λ(x) are constructed on their basis.

2. All isotherms λ(x) revealed an interval (x = 0.005-0.01) of abnormal growth in λ, the presence of which is associated with critical phenomena that accompany the transition.

3. It is shown that at room temperature, an abnormal increase in thermal conductivity leads to a decrease in TE figure of merit Z in the range of compositions near the critical (x = 0.01). Maximum value of Z obtained in the region of concentrations under study corresponds to the composition x = 0.07 and is $Z = (2.1 \pm 0.2) \cdot 10^{-3}$ K^{-1}.

4. The detected concentration anomalies of TE properties accopanying the transition from dilute to concentrated solid solutions should be considered when interpreting experimental results and practical applications of solid solutions of $Bi_2(Te_{1-x}Se_x)_3$, and other solid solutions.

Further studies of this system would include the investigation of the temperature dependences of the Seebeck coefficient and electrical conductivity, and the construction of isotherms of these properties in the range of compositions (x = 0-0.07). This will reveal how the effect of concentration anomalies on the thermoelectric Q-factor of $Bi_2(Te_{1-x}Se_x)_3$ will change with a change in temperature.

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Теплопровідність твердих розчинів $Bi_2(Te_{1-x}Se_x)_3$ (x = 0-0.07)

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Анотація

Актуальність. Тверді розчини $Bi_2(Te_{1-x}Se_x)_3$ – це ефективні матеріали для *n*-гілки термоелектричних охолоджуючих пристроїв. Нещодавно в цих твердих розчинах були виявлені концентраційні аномалії властивостей за малого вмісту домішки ($x \sim 0.01$). Важливо встановити, чи будуть аналогічні аномалії спостерігатися на залежності теплопровідності λ від складу твердого розчину, оскільки λ є одним із параметрів, що визначає термоелектричну добротність матеріалу.

Мета. Метою цієї роботи було дослідження концентраційних залежностей теплопровідності ТР $Bi_2(Te_{1-x}Se_x)_3$ в інтервалі x = (0-0.07) для виявлення концентраційних аномалій та їх можливого впливу на ТЕ ефективність.

Методологія. Дослідження температурних залежностей теплопровідності λ проводили методом динамічного калориметра. На їх основі побудовані ізотерми λ для різних температур в інтервалі T = 175-400 К.

Результати. На ізотермах λ спостерігається інтервал аномального зростання λ, яке стає більш вираженим при зниженні температури. Наявність цього інтервалу пов›язується з критичними явищами, що супроводжують перехід перколяційного типу від розведених до концентрованих твердих розчинів.

Висновки. Надана оцінка термоелектричної добротності Z матеріалів. Показано, що виявлене зростання λ призводить до зменшення Z в інтервалі складів поблизу критичного (x = 0.01), що необхідно враховувати при практичному застосуванні твердих розчинів $Bi_2(Te_{1-x}Se_x)_3$

Ключові слова: термоелектричні матеріали V_2VI_3, теплові властивості, склад, перколяція, термоелектрична добротність