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EFFECT OF DEVIATION FROM STOICHIOMETRY ON THERMAL CONDUCTIVITY OF Bi_2Se_3 POLYCRYSTALS

The dependences of electronic and lattice thermal conductivity on the composition (59.9 - 60.0) at. % Se of Bi_2Se_3 polycrystals subjected to a long-term annealing at 650 K. A non-monotonic behavior of these concentration dependences, associated with a change in the phase composition and defect structure under the deviation from stoichiometry, was observed. The boundaries of the Bi_2Se_3 homogeneity region were estimated. The results of the present work confirm those obtained earlier in our study of the effect of deviation from stoichiometry (59.9 - 60.0 at.% Se) on the electrical conductivity, Hall coefficient, Seebeck coefficient and microhardness of Bi_2Se_3 polycrystals after a similar preparation technology. Bibl. 33. Fig. 3.
Keywords: *bismuth selenide, stoichiometry, concentration, defect structure, thermal conductivity*

Introduction

Solid solutions based on the bismuth selenide are the well-known *n*-type thermoelectric (TE) materials for cooling devices [1]. Bi_2Se_3 belongs to a narrow-gap semiconductor group and demonstrates the unique properties of topological insulator (material which is dielectric in the bulk with a metallic layer on the surface) [2]. The efficiency of a TE energy convertor depends on the value of TE figure of merit Z of a TE material ($Z = S^2 \cdot \sigma/\lambda$, where σ and λ are the electrical and thermal conductivities, respectively, S is the Seebeck coefficient).

Bi_2Se_3 is a bertollide [3-5] with the homogeneity region (HR) shifted to the Bi-rich side at $T >$ 675 K [6]. Bi_2Se_3 melts congruently with an open maximum at 979 K [3,7,8], which is deviated from stoichiometry and located at (59.98 ± 0.01) at. % Se [3-6,9].

Bi_2Se_3 always exhibits *n*-type conductivity which is commonly associated with the presence of a large number of Se vacancies (V_{Se1}) [5,6,10-21] acting as donors. The existence of V_{Se1} was confirmed by a number of authors [6,12,15-18,22-24] with the help of different experimental and theoretical methods (scanning tunneling microscopy, measurements of the Hall coefficient in the temperature range 80-330 K, calculation of the formation energies of various types of defects etc.). Later [24-26], the coexistence of V_{Se1} and antisite defects (AD) – bismuth atoms that occupy positions of selenium ones (Bi_{Se}), in the *n*-Bi_2Se_3 was suggested.

The deviation from stoichiometry in chemical compound leads to the appearance of intrinsic defects, the concentration of which varies within the HR of the compound which determines the properties of the TE material. Analysis of the literature showed, that the HR boundaries of the Bi_2Se_3 were determined just for temperatures above 675 K [6], and the boundaries of the maximal HR are (59.984 - 59.997) at.% Se at 900 K. Despite the fact that Bi_2Se_3 is used for TE applications at

temperatures close to room temperature, the investigation of the HR boundaries at these temperatures are not available in the literature. In our previous work [27], based on the study of the electrical conductivity, Hall coefficient, Seebeck coefficient and microhardness of Bi_2Se_3 polycrystals with deviation from stoichiometry to the Bi-rich side after a long-term annealing at 670 K with subsequent cooling to the room temperature, the HR boundaries were estimated. The investigation of the thermal properties of such crystals could expand the range of research, supplement and/or confirm the results of [27]. As far as we know, no study of the thermal properties of Bi_2Se_3 polycrystals under the deviation from stoichiometry has been performed yet.

The typical values of λ for Bi_2Se_3 single crystals lie within 2.5-3.1 $W \cdot m^{-1} \cdot K^{-1}$ [12,28,29] and for pressed polycrystals – within 1.0-1.3 $W \cdot m^{-1} \cdot K^{-1}$ [30-32]. It is also known, that usually electronic component of thermal conductivity is comparable to the lattice one in single [28] and pressed [33] crystals. The values of $Z = 5 \cdot 10^{-4}$ K^{-1} [29] and $Z = 1.6 \cdot 10^{-4}$ K^{-1} [33] at a room temperature are typical for single and polycrystals Bi_2Se_3, respectively.

The purpose of the work was to study the effect of deviation from stoichiometry on the thermal conductivity and TE figure of merit of Bi_2Se_3 polycrystals at a room temperature.

Experimental

Bi-Se polycrystals with different Se concentrations (59.9 - 60.0) at. % were prepared by fusing high-purity (99.999 at. % of the main component) Bi and Se in evacuated quartz ampoules at a temperature of T = (980 ± 10) K. The melt was kept at this temperature for 3 h with vibrational stirring. After that the alloys were annealed for 200 h at T = 820 K with subsequent cooling to room temperature in the turned-off furnace. The synthesized alloys were used for subsequent preparing of powders for pressing with particle size of 200 μm. Pressed samples were prepared by cold-pressed method at a fixed load of 400 MPa for 60 s with subsequent homogenizing annealing in evacuated quartz ampoules at 650 K for 250 h with subsequent cooling to room temperature.

The thermal conductivity λ was measured by the dynamic λ-calorimeter method in monotonic heating regime with help of IT-λ-400 experimental facility. The errors of λ measurement did not exceed ± 5 %. The measurements were carried out at a room temperature.

The determination of the lattice component λ_{ph} of thermal conductivity was determined by subtracting the electronic component λ_{el} from the total thermal conductivity. The λ_{el} values were calculated with the help of the Wiedemann-Franz law:

$$\lambda_{el} = L\sigma T ,$$

where L is the Lorenz number ($L = 2.44 \cdot 10^{-8}$ V^2/K^2 for degenerate statistics), T is the temperature. The values of σ obtained in our previous work [27] for Bi_2Se_3 polycrystals with a deviation towards the excess of Bi after a similar preparation technology were used for calculation of λ_{el}.

Experimental results and discussion

The investigated polycrystals were homogeneous in its chemical composition and properties [27].

The obtained room-temperature dependence of λ on the composition of the Bi-Se pressed crystals is shown in Fig. 1.

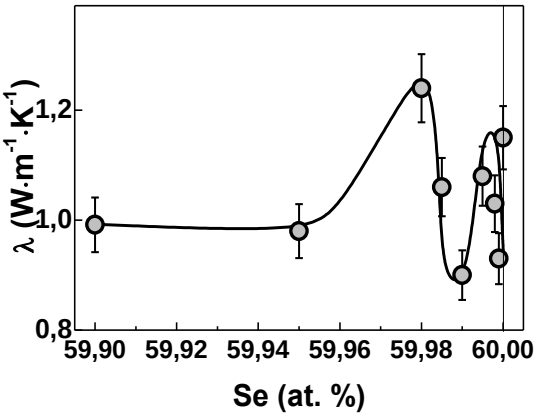

Fig. 1. Room-temperature dependence of thermal conductivity λ on Se content in Bi-Se polycrystals

The results of calculation of λ_{el} and λ_{ph} for Bi-Se polycrystals with different composition are shown in Fig. 2.

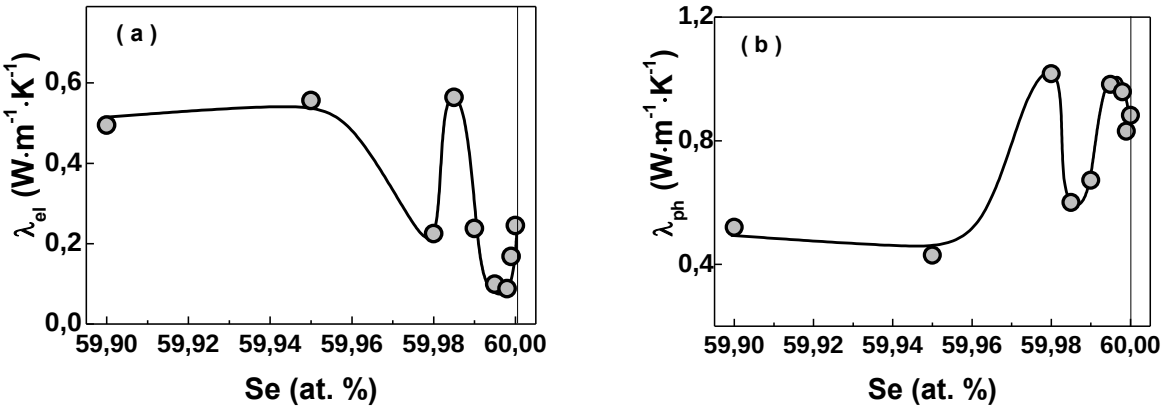

Fig. 2. The dependences of electronic λ_{el} (a) and lattice thermal conductivity λ_{ph} (b) on Se content in Bi-Se polycrystals

The calculation of the value of the TE figure of merit of Bi_2Se_3 crystals with an excess of Bi for different composition was made using the values of σ and S, obtained in our previous work [27], and λ, obtained in the present work (Fig. 3).

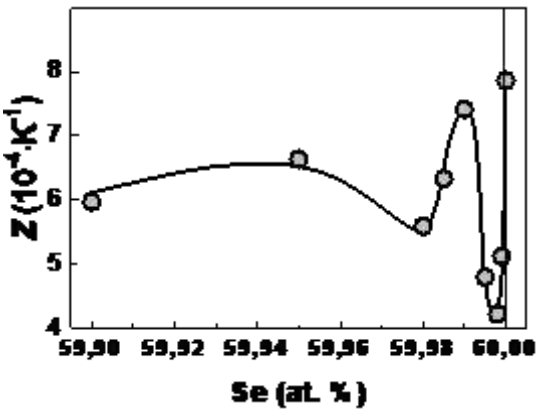

Fig. 3. The dependence of the TE figure of merit Z on Se content in Bi-Se polycrystals

As can be seen from Fig. 1 and Fig. 2, under the deviation from the stoichiometry of Bi_2Se_3 to the Bi-rich side, general trends of increasing in λ_{el} and decreasing in λ and λ_{ph} are observed. Starting from ~ 59.95 at.% Se, the values of λ_{el}, λ and λ_{ph} practically do not change. In the composition range (59.95–60 at.% Se) the concentration dependences of the thermal conductivity and its components are non-monotonic and exhibit an oscillating behavior. From Fig. 1 and Fig. 2 one can identify five regions with different dependence behaviors of properties on Se content:

1) 60.0 - 59.998 at.% Se, where λ_{el} tends to decrease, and λ and λ_{ph} tend to increase;

2) 59.998- 59.985 at.% Se, where λ_{el} increases, λ and λ_{ph} decrease;

3) 59.985- 59.98 at.% Se, where λ_{el} decreases, λ and λ_{ph} increase again;

4) 59.98 - 59.95 at.% Se, where increase in λ_{el} and decrease in λ and λ_{ph} are observed;

5) 59.95 - 59.90 at.% Se, where λ_{el}, λ and λ_{ph} do not change.

It should be noted that behavior of σ (see [27]) and λ_{el} (Fig. 2) on concentration coincide. This is logical, because λ_{el} is determined by the values of σ. The dependences of λ_{el} and λ_{ph} on the composition have an opposite character: the positions of observed maxima of the λ_{el} correspond to the positions of the minima of λ_{ph}.

A complicated behavior of the concentration dependences of compound properties under the deviation from stoichiometry indicates the crossing of the phase boundary. But within the HR, which is a single-phase region, such a behavior can indicate the self-organization processes in the compound and be determined by the redistribution of atoms and non-stoichiometric defects. Taking into account the long-term isothermal annealing at 650 K carried out for Bi-Se polycrystals after its pressing, one can assume that a phase state close to the equilibrium state at 650 K was reached and the subsequent cooling in the turned-off furnace to room temperature does not change this state.

According to the phase diagram of Bi-Se [3,4,6], a two-phase region (Bi_2Se_3 + Se) under the deviation from stoichiometry to the Bi-rich side should exist at a temperature T > 675 K. At temperature decrease below 675 K, the phase boundary may be shifted. Taking into account the trend of the boundary shifting with temperature decrease from 900 K to 675 K [3,6], the shift of phase boundary is most likely to occur at a lower Se concentration. So, it assumed that the first concentration range 60.0–59.998 at.% Se corresponds to the two-phase region (Bi_2Se_3 + Se), which is in the state of decomposition of the solid solution. In this region, many different factors affect the character of the composition dependences of properties (for example, the number and size of precipitated particles, cooling rate, etc.).

In the second region (59.998 - 59.985 at.% Se) we could expect the reaching of the HR boundary of Bi_2Se_3 from the Se-rich side. We can assume that subsequent deviation from stoichiometry towards the Bi excess in this region leads to V_{Se1} increase, which are electrically active defects and cause an increase in electron concentration (λ_{el} increases) and creates additional centers of phonon scattering in the lattice (λ_{ph} decreases).

The further deviation from stoichiometry (region 59.985 - 59.980 at.% Se) should result in further increase in the concentration of non-stoichiometric defects. It can be assumed, that the formation of an another type of non-stoichiometric defects – acceptor type AD (Bi_{Se}) [18,24] – becomes thermodynamically favorable. The appearance of Bi atoms at Se positions can lead to an increase in λ_{ph}. Taking into account that Bi_{Se} defects provide acceptor effect [18,23,24], these defects can partially compensate the donor action of V_{Se1} and lead to the decrease in λ_{el} in this region.

The next concentration region 59.98 - 59.95 at. % Se (λ_{el} increases, λ and λ_{ph} decrease) presumably corresponds to the reaching of the boundary of the Bi_2Se_3 HR from the Bi-rich side.

Further practically unvaried values of thermal properties of crystals in the range 59.95 - 59.90 at.% Se, most probably, indicate the precipitation of a second phase BiSe [3] upon crossing the solidus line.

Thus, based on the analysis of the obtained experimental data (Fig. 1, Fig. 2) we assumed that the boundary of the Bi_2Se_3 HR on the Bi-rich side lies in the range 59.98 - 59.95 at.% Se, and on the Se-rich side corresponds to ~ 59.998 at% Se. It should be noted that the HR boundaries of the Bi_2Se_3 and the character of change in the defect structure, experimentally determined in the present work, coincide and add further confirmation of the results of our earlier work [27].

Analysis of calculated electronic and lattice components of λ shows that the contribution of electronic component for all investigated samples is close to the lattice one. It should be also noted that under the deviation from stoichiometry to the Bi-rich side the contribution of λ_{ph} to the total thermal conductivity becomes smaller (see Fig. 2b). It is logical to associate this tendency with creation of different types of crystal defects. The latter indicates that phonons scatter strongly on defects (presumably, Bi_{Se} and V_{Se1}).

It should be noted that the value of λ_{ph} for the stoichiometric crystal (λ_{ph} = 0.85 $W \cdot m^{-1} \cdot K^{-1}$) was slightly lower than the data available in the literature (λ_{ph} = 1.07 $W \cdot m^{-1} \cdot K^{-1}$ [32]) for pressed crystals. This difference in the values of λ_{ph} could be explained by a different method of preparing samples (spark-plasma sintering at a temperature of 593 K for 5 min at a uniaxial pressure of 40 MPa was used in [32]).

As can be seen from Fig. 3, the value of Z also exhibits a non-monotonic type of dependence on the Se content in Bi-Se polycrystals. It can be seen that the largest value of $Z = 8 \cdot 10^{-4}$ K^{-1} is inherent in a crystal with the stoichiometric composition, and even under a slight deviation from the stoichiometry towards the Bi excess (59,998 at.% Se), the value of Z drops sharply ($Z = 4.2 \cdot 10^{-4}$ K^{-1}), which is important from a practical point of view. It should be noted that the values of Z obtained here for Bi-Se crystals at a room temperature were slightly higher than those known in the literature for pressed stoichiometric Bi_2Se_3 [29,33]. This gain in the value of Z is a consequence of the lower value of λ and the higher value of S [27] of the crystal, which was subjected to a long-term annealing at 650 K with subsequent cooling to room temperature in the turned-off furnace in the present work, compared with the literature data [29,33] for the pressed crystals.

Conclusions

The effect of the deviation from stoichiometry to the Bi-rich side (59.9–60.0) at. % Se on the electronic and lattice components of thermal conductivity of the Bi_2Se_3 polycrystals was studied. The boundaries of the Bi_2Se_3 homogeneity region (on the Se-rich side – 59.998 at. % Se, and on the Bi-rich side – in the interval of 59.98–59.95 at. % Se) after a long-term annealing at 650 K with subsequent cooling to the room temperature were estimated.

The estimated HR boundaries of Bi_2Se_3 confirm the previous results [27] in the analysis of the concentration dependences of the electrical conductivity, Hall coefficient, Seebeck coefficient and microhardness.

The non-monotonic behavior of the concentration dependences of the electronic and phonon thermal conductivities at a room temperature attributed to a change in the phase composition and defect structure under the deviation from stoichiometry of Bi_2Se_3 was observed. It is supposed that within the homogeneity region with the dominant type of non-stoichiometric defects (selenium vacancies) the formation of antisite defects Bi_{Se} occurs.

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ВПЛИВ ВІДХИЛЕННЯ ВІД СТЕХІОМЕТРІЇ НА ТЕПЛОПРОВІДНІСТЬ ПОЛІКРИСТАЛІВ Bi_2Se_3

Отримано залежності електронної та граткової теплопровідності від складу (59.9 - 60.0 ат. % Se) полікристалів Bi_2Se_3 після довготривалого відпалу за температури 650 К. Виявлено немонотонний характер цих залежностей, який пояснюється зміною у фазовому складі та дефектній структурі при відхиленні від стехіометрії. Зроблено оцінку меж області гомогенності Bi_2Se_3. Результати даної роботи підтверджують результати, які були отримані нами раніше при дослідженні впливу відхилення від стехіометрії (59.9 - 60.0 at. % Se) на електропровідність, коефіцієнт Холла, коефіцієнт Зеєбека та мікротвердість полікристалів Bi_2Se_3 після аналогічної технології приготування. Бібл. 33, рис. 3.
Ключові слова: селенід вісмуту, стехіометрія, концентрація, дефектна структура, теплопровідність

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ВЛИЯНИЕ ОТКЛОНЕНИЯ ОТ СТЕХИОМЕТРИИ НА ТЕПЛОПРОВОДНОСТЬ ПОЛИКРИСТАЛЛОВ Bi_2Se_3

Получены зависимости электронной и решеточной теплопроводности от состава (59.9 - 60.0 ат.% Se) поликристаллов Bi_2Se_3 после длительного отжига при температуре 650 К. Обнаружен немонотонный характер этих зависимостей, который объясняется изменением в фазовом составе и дефектной структуре при отклонении от стехиометрии. Произведена оценка границ области гомогенности Bi_2Se_3. Результаты данной работы подтверждают результаты, полученные нами ранее при исследовании влияния отклонения от стехиометрии (59.9 - 60.0 at.% Se) на электропроводность, коэффициент Холла, коэффициент Зеебека и микротвердость поликристаллов Bi_2Se_3, изготовленных по аналогичной технологии. Библ. 33, рис. 3.
Ключевые слова: селенид висмута, стехиометрия, концентрация, дефектная структура, теплопроводность

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