The resistivity, Seebeck coefficient and thermal diffusivity were determined for Bi$_2$Te$_3$ + Ag$_2$Te composite mixtures. Subsequent measurements were carried out in the temperature range from 20 to 270°C, and for compositions from pure Bi$_2$Te$_3$ to x$_{Ag_2Te}$ = 0.65 selected along the pseudo-binary section of Ag-Bi-Te ternary system. It was found that conductivity vs. temperature dependence shows visible jump between 140 and 150°C in samples with highest Ag$_2$Te content, which is due to monoclinic $\Rightarrow$ cubic Ag$_2$Te phase transformation. Measured Seebeck coefficient is negative for all samples indicating they are n-type semiconductors. Evaluated power factor is of the order 1.52·10$^{-3}$ and it decreases with increasing Ag$_2$Te content (at. %). Recalculated thermal conductivity is of the order of unity in W/(m K), and is decreasing with Ag$_2$Te addition. Finally, evaluated Figure of Merit is 0.43 at 100°C and decreases with temperature rise.

Keywords: thermoelectric materials; Seebeck coefficient; resistivity; thermal diffusivity; Bi$_2$Te$_3$-Ag$_2$Te system

Introduction

In 1821-3 Thomas Seebeck discovered [1] that when a closed circuit made of two different metals A and B is placed in the temperature gradient, this temperature difference produces a current flowing through the circuit. This phenomenon, called today Seebeck effect, was the first demonstration that the heat flux and the flow of electrons are coupled. When this circuit is broken, and the junctions between dissimilar metals are held at different temperatures, electric potential difference is produced between created this way terminals. Moreover, this voltage is proportional to the temperature difference imposed between two junctions. The proportionality constant is called Seebeck coefficient, and the whole effect can be described by the simple relation:

$$\Delta V = \frac{\alpha_{A/B}}{\Delta T}$$

where $\Delta V$ is generated potential difference which is called thermoelectric force, $\Delta T$ is imposed temperature difference between two junctions, and $\frac{\alpha_{A/B}}{}$ is Seebeck coefficient ($\frac{\Delta V}{\Delta T}$) measured in Volts per Kelvin.

It is clear from eq. 1 that produced thermoelectric force $\Delta V$ depends not only on $\Delta T$ but also on $\frac{\alpha_{A/B}}{}$, which in turn depends on a chosen material. The value of the coefficient $\alpha$ can be either positive or negative, depending on either holes or electrons conduction. Moreover, it depends also on the reference material. Usually metallic Pt is used as the reference in Seebeck coefficient determination. In such a case, the reference value is set to zero. Thus, to obtain the highest possible thermoelectric force from the source of heat, one must apply materials yielding highest value of Seebeck coefficient. Obviously, the heat (most important – waste heat) can be converted into electricity directly, and it is the reason why thermoelectric effect has attracted today so much attention. It can be exploited not only in thermocouples used in various temperature controlling devices, but also in large variety of other technological applications. Recent advances in this field as well as materials and their applications were described by Tritt and Subramanian [2], and Snyder and Toberer [3]. Numerous examples of technological applications can be mentioned, and some of them are given below. It appears that thermoelectric materials (Te) can be used in:

- converting the waste heat from vehicle exhaust into electric power [4],
- maintaining cathodic protection of oil drilling platforms [5],
- stabilizing operating wavelength of laser diodes [6],

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rerecovering industrial waste-heat in aluminium smelting [7],
• powering space vehicles like Voyager and Cassini during NASA missions, as well as Curiosity rover on Mars [8,9].
For space missions electrical power was obtained by converting heat generated by 233U isotope.
In order to optimize the performance of a thermoelectric material Abram Ioffe [10] developed the concept of dimensionless Figure of Merit, $zT$. It describes the maximum efficiency of a thermoelectric material for conversion of the heat flow into electricity, and is given by the following relation:

$$ ZT = \frac{\alpha^2 \sigma T}{\kappa} $$

where $\alpha$ is Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is thermal conductivity (which is the sum of lattice and electronic contributions $\kappa_l + \kappa_e$), and $T$ is the temperature. The higher value of $zT$ one obtains, the better thermoelectric material it is.

It is clear from eq. (2) that maximization of $zT$ requires materials with high electrical conductivity, large Seebeck coefficient and small thermal conductivity. These requirements are contradictory. High electrical conductivity is characteristic for metallic conductors, but experiments conducted with metallic thermocouples indicate that $\alpha$ is small (typically 10-60 $\mu$V/K). Thus, to increase Seebeck coefficient, a material with lower conductivity is required. It can happen if charge carriers are slow, or carrier concentration decreases. Theoretical considerations showed [11], that $\alpha$ depends not only on the number of carriers but also on their effective mass. Higher mass can be related to the density of states and energy band gap of a material. In general, $\alpha$ is proportional to energy per charge carrier, relative to Fermi level. Thus, it is dependent on temperature and electronic structure of the material. Mahan and Sofo [12] suggested that a good candidate for thermoelectric material is a narrow-bandgap semiconductor, for which the product $\sigma \alpha$ (called power factor) can be optimized by doping.

The numerator in eq. (2) is divided by thermal conductivity, which should be low to enhance $zT$. Since $\kappa$ is determined by electrons (holes) as well as phonon movements, its low value is in conflict with the requirement for the material to exhibit high electronic conductivity. Fortunately, very low thermal conductivity may be achieved when crystal lattice is able to scatter phonons. Indeed, a kind of unusual material is needed for the best thermoelectric scatter phonons. Fortunately, very low thermal conductivity may be achieved when crystal lattice is able to inhibit high electronic conductivity. It was soon discovered that $\alpha$ is small (typically 10-60 $\mu$V/K).

In the past, the first thermoelectric material used by Goldsmid and Douglas in industrial application [19] was Bi2Te3. Bismuth telluride is $n$-type semiconductor with Seebeck coefficient $-230 \mu$V/K [20]. It has two-dimensional layered structure, which is rhombohedral-hexagonal. It was soon discovered that alloying Bi2Te3 with chalcogenides of antimony, lead tin, and germanium one can obtain even better thermoelectric material [21]. Unfortunately, ternary Pb-Ge-Se alloys with the highest Seebeck coefficient [20] contain lead and selenium which are considered to be toxic. Consequently, some alternatives were found which contain silver [22-24], copper [25-27]. For example, ternary chalcogenide AgSbTe2 with GeTe addition (TAGS) has reached $zT$ value above one [28].

Silver (I) telluride is itself an interesting electric material. Ag2Te has three-dimensional monoclinic structure. At room temperature it is narrow band-gap semiconductor. As temperature increases it undergoes two phase transitions: monoclinic $\leftrightarrow$ a at 145°C, and $\alpha$-fcc $\leftrightarrow$ $\beta$-bcc at 802°C. The first phase transition changes its transport properties into superionic conductor. Electronic properties of $\alpha$- and $\beta$-Ag2Te were investigated from room temperature to about 630°C by Fujikane et al. [29]. They found that electrical resistivity changes at about 147°C, i.e. around monoclinic $\leftrightarrow$ a transition. Calculated power factor suggests that it is better to use $\alpha$-Ag2Te as a thermoelectric material. Ouyang et al. [30] analysed thermal transport properties of $\alpha$-Ag2Te using molecular dynamic simulations. They found that

![Fig. 1. Figure of Merit $zT$ vs. temperature plot after Zabek and Morini [18]](image-url)
thermal transport in this phase results mainly from vibrations in Te\textsuperscript{2\textendash} sublattice, while interactions between Ag\textsuperscript{+} and Te\textsuperscript{2\textendash} ions hinder the heat transfer. It was also shown in that work \[30\] that stoichiometry of Ag\textsubscript{2}Te compound has the influence on thermal conductivity. Silver deficient compound exhibits lower thermal conductivity. This study indicates directions one should take to lower thermal conductivity of a material. Selecting the crystal structure, controlling interactions between unlike ions and controlling stoichiometry by doping one have an influence on thermal conductivity. This is consistent with the theory of thermoelectricity summarized by Zhang and Zhao \[31\]. Ag\textsubscript{2}Te is an important thermoelectric material due to its properties and therefore is combined with other thermoelectric materials that can increase the $zT$ factor.

Another factor which can be varied is the size. Lee et al. \[32\] investigated thermoelectric properties of synthesized single crystalline Ag\textsubscript{2}Te nanowires. They observed that when Ag\textsubscript{2}Te phase changes into cubic structure, power factor suddenly decreases. It suggests the increased density of states of electrons due to the nanowire structure. It seems that silver (I) telluride is an interesting material which can be used in thermoelectrics. However, some attempts have been made to mix it with other thermoelectric materials based on bismuth telluride. For example Lee et al. \[33\] investigated thermoelectric properties of Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3}/Ag\textsubscript{2}Te bulk composites with size- and shape-controlled Ag\textsubscript{2}Te nano-particles dispersion, Sakakibara et al. \[34,35\] measured thermoelectric properties for AgBiTe\textsubscript{2}/Ag\textsubscript{2}Te composites, Fang et al. \[36\] investigated thermoelectric properties of silver telluride-bismuth telluride nanowire heterostructure. Since the influence of Ag\textsubscript{2}Te addition on thermoelectric properties of Bi\textsubscript{2}Te\textsubscript{3} has not been reported so far, it was decided to investigate thermoelectric properties of alloys in Ag\textsubscript{2}Te – Bi\textsubscript{2}Te\textsubscript{3} pseudo-binary system. Thus, the aim of this paper is to measure the resistivity (reciprocal conductivity), Seebeck coefficient and thermal diffusivity, and then to determine power factor and the Figure of Merit $zT$ of Ag\textsubscript{2}Te-Bi\textsubscript{2}Te\textsubscript{3} alloys as a function of temperature and alloy composition.

**Materials and experimental methods**

Samples of Ag-Bi-Te alloys were synthesized by using SPS method. Powders of Bi\textsubscript{2}Te\textsubscript{3} (99.98% pure, obtained from Alfa Aesar) and Ag\textsubscript{2}Te (obtained from Sigma Aldrich) were ground first in the ball mill (Fritsch, Pulverisette 23, the container and balls made of ZrO\textsubscript{2}). This procedure equalized diameters of grains of the initial materials before their mixing. Next, the alloy samples with the compositions given in Tab. 1 were prepared by mixing these powders. Compositions of six alloys were selected along the pseudo-binary section Ag\textsubscript{2}Te-Bi\textsubscript{2}Te\textsubscript{3} of the ternary Ag-Bi-Te system.

Prepared samples were introduced into sintering apparatus Dr Sinter, Spark Plasma Sintering System, model SPS – 515S, SPS Syntex Inc. (Kanagawa, Japan). The powders were placed into graphite die ($d = 10$ mm, $h = 3$ mm). Before powder introduction, a graphite disc was placed on the bottom of the matrix to separate the powder from the press piston. Similar disc was placed from above to cover the powder. The sintering took 5 min at the temperature 400°C and under pressure of 50 MPa. The rate of heating was set to 50°C/min. After sintering samples were analysed by X-ray to check their final phase composition. The phase composition of studied alloys was determined by X-ray Powder Diffraction (XRD) method using Rigaku Japan MiniFlex II X-ray Diffractometer with Cu-Kα radiation. Next, to check stability of prepared samples, small portion of each was subjected to TGA analysis. These experiments were conducted on Netzsch.

<table>
<thead>
<tr>
<th>No Sample</th>
<th>Sample composition [at. %]</th>
<th>$x_{\text{Ag}_2\text{Te}}$</th>
<th>$x_{\text{Bi}_2\text{Te}_3}$</th>
<th>XRD results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Bi40Te60</td>
<td>0</td>
<td>1</td>
<td>Bi\textsubscript{2}Te\textsubscript{3} 00-015-0863</td>
<td></td>
</tr>
<tr>
<td>2 Ag05Bi37Te58</td>
<td>0.119</td>
<td>0.881</td>
<td>Bi\textsubscript{2}Te\textsubscript{3} 01-076-2813</td>
<td></td>
</tr>
<tr>
<td>3 Ag10Bi34Te56</td>
<td>0.227</td>
<td>0.773</td>
<td>Ag\textsubscript{2}Te 01-081-1186</td>
<td></td>
</tr>
<tr>
<td>4 Ag17.5Bi29.5Te53</td>
<td>0.372</td>
<td>0.628</td>
<td>Ag\textsubscript{1.85}Te 00-018-1186</td>
<td></td>
</tr>
<tr>
<td>5 Ag25Bi25Te50</td>
<td>0.500</td>
<td>0.500</td>
<td>Ag\textsubscript{1.85}Te 01-015-0863</td>
<td></td>
</tr>
<tr>
<td>6 Ag35Bi19Te46</td>
<td>0.648</td>
<td>0.352</td>
<td>Ag\textsubscript{1.85}Te 00-018-1186</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1 Composition of Ag-Bi-Te alloys along the pseudo-binary section Ag\textsubscript{2}Te-Bi\textsubscript{2}Te\textsubscript{3} of the ternary Ag-Bi-Te system, mole fractions of Ag\textsubscript{2}Te and Bi\textsubscript{2}Te\textsubscript{3} compound in the samples and experimental results (XRD data) for prepared samples
Samples for thermoelectric properties measurements were prepared from samples obtained by SPS method. Small cuboids of dimensions \( l = 10 \text{ mm}, w = 2.8-3.0 \text{ mm} \) and \( h = 0.9 – 1.55 \text{ mm} \) were cut off from sintered samples. Determination of resistivity \( \rho \) and Seebeck coefficient \( \alpha \) was conducted on ZEM-3, ULVAC Co. Ltd (Japan) apparatus. In order to measure the resistivity and Seebeck coefficient, the investigated sample is placed between the upper and lower blocks in the heating furnace. The heater in the lower block provides the temperature gradient. In this off-axis four point geometry, thermocouples are pressed against the side of the sample, and they measure four point geometry, thermocouples are pressed against the side of the sample. \( T_1 \) and \( T_2 \) temperatures at two different points (i.e. they establish temperature gradient \( \Delta T \)). The surface of the samples was carefully polished to assure good thermal and electrical contacts. The voltage difference between two alike wires of these two thermocouples is measured yielding thermoelectric force \( \Delta V \). Experiments were carried out in the temperature range from 20 to 270°C under helium at the pressure \( 10^{-1} \text{ MPa} \). Temperature was varied in steps of 20 degree, and measurements were taken when selected temperature difference was attained before each measurement. The device is operating in a steady-state mode in which measurements are taken after stabilization of the temperature gradient. Voltage drop \( E \) is measured at the same two points of the sample and between the same alike thermocouple wires. After correcting this voltage drop for thermoelectric force \( \Delta V \) generated by temperature gradient, the resistance of the sample can be determined. Having the distance between tips of these two thermocouples and the sample geometry, specific resistivity (conductivity) can be derived. In this way both, Seebeck coefficient and resistivity of the sample were determined.

Thermal diffusivity \( D_T \) (in \( \text{cm}^2/\text{s} \)) was determined by using laser flash method with the apparatus Netzsch LFA 457 (Germany). In this experimental setup the thin sample (about 10 mm in diameter and 1-2 mm in thickness) is exposed to the short laser pulse (pulse energy 5 to 8 J) from the bottom, while its temperature is monitored from above by an infrared (IR) detector. The sample is placed in thermal shield to eliminate radial heat losses, and to assure one-dimensional heat flow. The pulse of energy is absorbed by the sample’s surface, and the temperature change of the sample versus time is recorded on the other side of the sample to determine its maximum rise. Parker et al. [37] developed the model which does not require the knowledge of received energy pulse. Assuming adiabatic case, thermal diffusivity is proportional to the ratio \( (T_2^2 - T_1^2)/T_{1/2} \), where \( T_{1/2} \) is the time necessary for the temperature to rise to \( 1/2 \) of its maximum. Parker’s model was later improved by Cowan [38], who took into account heat losses due to radiation and convection on the surface. This correction has been implemented in the software operating with the device. The whole experimental setup is placed in a furnace to carry on measurements at different temperatures. Obtained data on the heat diffusivity can be converted into thermal conductivity \( \kappa \) (in \( \text{W/cm K} \)) with help of the relation [39]:

\[
\kappa = D_T d C_p
\]

where \( d \) is density [\( \text{g/cm}^3 \)] and \( C_p \) is specific heat capacity of the sample in \( \text{J/g K} \).

The microstructure of selected sintered samples was observed by scanning electron microscopy (SEM) (Hitachi, SU-70, Japan, with electron microprobe ThermoScientific, with ZAF correction). For qualitative and quantitative analysis the EDX (Energy Dispersive X-ray Spectroscopy) method was applied.

**Results**

The results of experimentally determined densities of respective samples are shown in Fig. 2, in which they are compared with theoretical density.

![Fig. 2. Bar graph of determined samples density as compared with its theoretical values.](image)

It may be seen that the maximum difference between theoretical and measured densities is (at average) of the order of 2% which fit in the experimental error range.

Results of X-ray analysis of the samples 1-6 prepared for subsequent measurements are shown in Fig. 3, while the results of this analysis are given in Table 1. Obtained results indicate that two-phase mixture was obtained for all samples. Additionally, new ternary phase AgBiTe\(_2\) is also identified in samples rich in Ag\(_2\)Te.

However, it must be mentioned that this phase is not present on the microstructure revealed by SEM and shown in Fig. 4.

The results of resistivity measurements were recalculated to obtain specific conductivity \( (\sigma = 1/\rho) \), which is shown in Fig. 5 as a function of temperature for different sample composition.
In the range 140-150°C the change in slope of this dependence is visible. This change is getting more pronounced with the increasing Ag₂Te content. It indicates the detection of the structural transformation of Ag₂Te which according to the binary Ag-Te phase diagram is equal to 145°C.

Similarly, Seebeck coefficient determined for different samples is shown as a function of temperature in Fig. 6.

Obtained values of the coefficient are negative for all samples which means they are n-type semiconductors. The value measured for Bi₂Te₃ is almost constant with temperature. The addition of Ag₂Te results in visible decrease of the coefficient (it roughly corresponds to doped Bi₂Te₃ around room temperature). It is also seen that the temperature increase results in the reduction of Seebeck coefficient towards more positive values.

Having determined Seebeck coefficient and the conductivity, the power factor \((σ \cdot α^2)\) was derived for two temperatures 100 and 262°C. These results are shown in Fig. 7 as a function of a sample composition. In general, increasing the Ag₂Te content reduces the power factor, while the increase of temperature has small effect on this change. The maximum value of the power factor determined in this study is \(1.52 \cdot 10^{-3}\) at 100°C and \(0.77 \cdot 10^{-3}\) at 262°C. This result is encouraging since to be applied in current devices, TE material should have the power factor of the order of \(10^{-3}\).
Fig. 6. Seebeck coefficient vs. temperature plots for samples 1-6: a) no. 1 – Bi40Te60, b) no. 2 – Ag05Bi37Te58, c) no. 3 – Ag10 Bi34Te56, d) no. 4 – Ag17.5Bi29.5Te53, e) no. 5 – Ag25Bi25Te50, f) no. 6 – Ag35Bi19Te46

Fig. 7. Power factor vs. sample composition evaluated at two temperatures 100 and 262°C

In order to obtain thermal conductivity, thermal diffusivity was measured and obtained results are shown in Fig. 8a. Next, they were recalculated using eq. 3. Density of respective samples was taken from this work. To calculate specific heat capacity, heat capacity data for Bi₂Te₃ and Ag₂Te were accepted after Kubaschewski, Alcock and Spencer [41]. The results of thermal conductivity calculations are shown in Fig. 8b.

It is obvious that the addition of Ag₂Te decreases thermal diffusivity, which however increases with temperature. This trend is observed for all samples. Moreover, there is a change in slope of this dependence which may suggest some changes in heat transfer mechanism. As far as thermal conductivity is concerned, it decreases with the silver telluride addition. The slope of temperature dependence increases with rising temperature. The jump resulting from phase transformation of Ag₂Te is also visible for alloys with highest Ag₂Te content.

Finally, the Figure of Merit, $zT$, was calculated and is shown in Fig. 9 for two temperatures 100 and 265°C as a function of the sample composition.

In turn, the dependence of the Figure of Merit on temperature is shown in Fig. 10.

It appears that increasing the temperature one can slightly reduce the Figure of Merit. It changes irregularly with Ag₂Te addition reaching maximum value 0.43 at 100°C, and 0.2 at 262°C (Fig. 9).
The very detailed analysis of possible experimental difficulties in thermoelectric transport properties measurements has been given recently by Borup et al. [42]. Thus, in this paper we are going to concentrate only on several points directly related to our experiments. The first requirement to obtain reliable results on thermoelectric properties of a material is careful sample preparation. Since Seebeck coefficient is sensitive to the presence of impurities, the purity of starting materials is of great importance. We used commercially available Bi$_2$Te$_3$ and Ag$_2$Te, which were 99.98% and 99% pure, respectively. Thus, introduction of some impurities into a final sample cannot be excluded. Application of SPS method of the sample synthesis gave product which after synthesis had density differing from theoretical density by about 2%. It is reasonable result, since it is in the range of deviations in which determined $zT$ value is still acceptable [43]. However, as a result of high-temperature synthesis, X-ray detected in samples a fraction of a new phase AgBiTe$_2$. It indicates the formation of a three-phase mixture, which apparently must affect the electronic properties of the product. The stoichiometry of this phase is identical with AgSbTe$_2$ and AgBiSe$_2$, which are known to exhibit good thermoelectric properties [29,44-46]. However, the stability and the range of existence of AgBiTe$_2$ is not so clear. Pseudo-binary Ag$_2$Te-Bi$_2$Te$_3$, section [47] of the ternary Ag-Bi-Te phase diagram indicates that this phase is stable only in narrow temperature range, i.e. from eutectoid reaction at 443°C to congruent melting between 555°C [48] and 557°C [49]. Thus, in the temperature range of our experiments it should not exist. Its presence is probably due to the nonequilibrium conditions during synthesis and it is metastable. Such a conclusion is supported by SEM analysis (Fig. 4) which did not revealed the presence of this ternary phase in the samples corresponding to their composition. Their controversy can be solved when careful investigations of phase equilibria in the ternary system Ag-Bi-Te will be conducted. At this moment it can be only speculated that presence detected by X-ray analysis has something to do with temperature, pressure or time of samples synthesis. Thus, either the reaction has not been completed (too short time), or fast decomposition of this phase took place. It would be very interesting to isolate this phase and to determine its thermoelectric properties. Its small range of stability could hinder this kind of experiment. However, alloying of AgBiTe$_2$ with another phases was conducted. For example, Sakakibara et al. [34,35] mixed AgBiTe$_2$ and Ag$_2$Te, synthesized by traditional melting method and carried out the measurements of the thermoelectric properties for these composites. Avramova and Plachkova [50] tested electrical resistivity for thermoelectric materials in the GeTe-AgBiTe$_2$ system. Tan et al. [51] combined SnTe and AgBiTe$_2$ compounds by melting and SPS methods and measured Seebeck coefficient, electrical conductivity, thermal conductivity and Hall mobility.

Measurements of resistivity and Seebeck coefficient were carried out simultaneously on a commercial setup. In their recent work de Boor and Muller [52] analyzed the errors committed most often during Seebeck coefficient determination. They pointed out that the main sources of errors are thermal contacts resistances, heat flux through thermocouples, but also the way how Seebeck coefficient is extracted from the raw data recorded during experiments. Simultaneous acquisition of the measured temperature and voltages also matters since there can be an interference from the heaters. In case of commercial equipment those problems depend on the construction of the device, data acquisition system and operating software. ZEM-3 has its own software provided with the apparatus. Thus, from the point of view of the experimenter, the greatest care must be taken during sample preparation (surface, dimensions) since the mode...
of device’s operation is fixed by the software. It should be only mentioned that in case of data comparison, reference material must be also taken into account. In our case it is constantan, while table’s values are usually given against Pt. In turn, the main error in the resistivity measurements seems to result from small differences in samples dimensions and quality of electrical contacts. These samples are small and it is difficult to make them identical. Also, non-homogeneity of sintered samples and their density may influence measured resistivity. Obtained results indicate Ag$_2$Te phase transition, which is visible in the range 140-150°C. It corresponds to monoclinic $\Rightarrow$ cubic transformation [40], and the change in slope of conductivity $\sigma$ vs. temperature $T$ dependence is more visible as Ag$_2$Te content increases.

Seebeck coefficient measured for Bi$_2$Te$_3$ is negative and slightly decreasing with temperature. This trend of the Seebeck coefficient is comparable to the trend of the curves for the plot of the Seebeck coefficient as a function of temperature in the work of Kim and Mitani [53]. Bi$_2$Te$_3$ samples were fabricated using hot pressing method [53]. In Kim and Mitani’s work [53] the values of the Seebeck coefficient are in the range of about –140 to –150 $\mu$V/K for the temperature range 0-27°C. The values of the Seebeck coefficient in this work are in the range between –95 and –105 $\mu$V/K for the temperature range of 0-300°C. The obtained values of the Seebeck coefficient are relatively comparable, taking into account the differences in the methods of sample synthesis, the grain size of the materials. The sample of pure Bi$_2$Te$_3$ was made of commercially available reagent and a possible influence from impurities is not known. However, large negative values of Seebeck coefficient can be observed at low temperature with Ag$_2$Te additions. This effect changes slightly with increasing temperature and simultaneous increase of electrical conductivity. At high temperature, silver telluride becomes superionic conductor and the change in conduction mechanism is possible. Moreover, silver telluride and Bi$_2$Te$_3$ react forming intermetallic phase AgBiTe$_2$ [49]. Though this phase is supposed not to exist below 443°C, its presence in samples is confirmed by X-ray studies. Unfortunately, thermophysical properties of this phase are not known and it’s hard to predict its influence on measured Seebeck coefficient.

Thermal conductivity was derived indirectly from measured thermal diffusivity and specific heat capacity calculated from thermochemical tables [41]. While linear approximation should work well for the mixture of two phases, the presence of AgBiTe$_2$ phase of unknown $C_p$ must affect the value of $C_p$ for the mixture. Thermal conductivity can be determined directly by e.g. DSC or drop calorimetry. However, this approach requires additional measurements on the same sample. It may be difficult since requirements of these two experiments can be quite different as far as dimensions of samples are concerned. There is another method based on LFA apparatus which makes use of maximum temperature rise, $T_{\text{max}}$, related to $C_p$ by the relationship:

$$C_p = \frac{Q}{m T_{\text{max}}}$$  \hspace{1cm} (4) $$

where $Q$ is a heat, $m$ is a mass. It requires however accurate determination of the amount of heat $Q$ absorbed by the sample. And it is not so obvious. This problem can be solved by the proper calibration with a material with well-known specific heat [54]. However, we used indirect method which may be acceptable if the sample consists of the mixture of two phases having well-known specific heat capacity. In our system this condition is almost fulfilled, but the presence of the ternary phase (its amount is not known) certainly introduces an error in final $C_p$ estimation.

Finally, power factor (which defines electrical performance of thermoelectric materials) and Figure of Merit (indicating maximum efficiency of TE material) has been evaluated (Fig. 9, 10). The maximum power factor found in this study is 1.52·10$^{-3}$ at 100°C, and maximum Figure of Merit is of the order of 0.43 at 100°C. Our findings are compatible with the results of Chen et al. [24] who studied a silver alloyed $n$-type Bi$_2$Te$_3$. They showed that the addition of Ag nanoparticles to Bi$_2$Te$_3$ nanopowder yields TE material with a Figure of Merit of 1.48 at room temperature. Thus, the reduction of the size of particles increased the Figure of Merit above 1.0 [24]. However, it is one of two studies of thermoelectric properties we found for Ag-Bi-Te alloys. In a second research, Fang et al. [36] investigated thermoelectric properties of silver telluride-bismuth telluride nanowire heterostructure. However, the research focused on the thermoelectric properties of nanomaterials and it is difficult to compare them with the properties of bulk materials. Moreover, two chemical compositions of the samples were investigated: 4.4 mol% and 15.2 mol% Bi$_2$Te$_3$ for the first and the second sample, respectively [36]. Therefore, there is no aspect to compare with this work. Whereby, the comparison with other data obtained for Ag-Bi-Te system is not possible at present.

A decrease of the $zT$ values is observed with the temperature increase in Fig. 10. The Figure of Merit values for pure Bi$_2$Te$_3$ are in the range of 0.23-0.27, which is quite a low result for this material. Bi$_2$Te$_3$ alloys, which are prepared by traditional zone melting method, have got $zT$ factor close to 0.8-1 [55,56]. Tang et al. [57] prepared Bi$_2$Te$_3$ bulk material with a layered structure by the melt-spinning and SPS processes and a maximum $zT$ of 1.35 was obtained at room temperature [57]. The $zT$ values are influenced by the Seebeck coefficient which depends on the concentration of the charge carriers. It has been observed that various methods of Bi$_2$Te$_3$ synthesis can cause to increase of electrically active defects in the polycrystalline form, which may be caused by charged defects at the non-equilibrium grain boundary or by expanded defects or unknown impurities [58]. For example, high energy ball milling [59,60] may have a donor-like effect. Annealing or other high temperature treatment (e.g. plasma spark sintering [59,61]) may reduce, but may not eliminate, the doping effect. In the materials fabricated in this way, the concentration of the charge carrier may change significantly, and as a consequence even cause the reversal of the dominant type of the charge carrier in relation to the growing composition [62,63]. Therefore, the applied methods of synthesis in this work might have an influence on the values of the Seebeck coefficient of the Bi$_2$Te$_3$ compound as well as Ag-Bi-Te alloys, and thus on the values of the $zT$ factor.
Conclusions

Summarizing the results of this work the following conclusions can be drawn:

- The Seebeck coefficient, resistivity, thermal conductivity, power factor and Figure of Merit \( zT \) of selected alloys in the Ag$_2$Te-Bi$_2$Te$_3$ pseudo-binary system were investigated for the first time.
- Up to 270°C all prepared samples consist of the mixture of two phases: Bi$_2$Te$_3$+Ag$_2$Te. For increasing amount of Ag$_2$Te the presence of ternary phase AgBiTe$_2$ becomes visible.
- Both initial components of these mixtures are \( n \)-type semiconductors. Above around 150°C in samples richer in Ag$_2$Te, conductivity exhibits jump due to the phase transformation, and slightly increases with temperature due to the change in charge transfer mechanism. Only in case of commercial Bi$_2$Te$_3$ a slow, steady decrease in conductivity with temperature is observed.
- Thermal conductivity increases with Ag$_2$Te addition, while the increase of temperature slightly accelerates this increase.
- The maximum power factor is of the order 1.52·10$^{-3}$ at 100°C and Figure of Merit is 0.43 at 100°C, and both parameters decrease with temperature.
- The study of phase equilibria in Ag-Bi-Te ternary system is necessary to assess the range of existence and the stability of respective phases. It is desirable to establish the temperature and composition range in which solid solutions and intermetallic phases may exist.

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