



Structural and Thermoelectric Properties of AgSbSe₂-AgSbTe₂ System

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Abstract

Nine compounds with nominal composition AgSbSe_xTe_{2-x} ($x = 0.00, 0.25, \dots, 2.00$) were synthesized by the direct fusion technique. The thermal analysis and X-ray diffraction revealed that a partial substitution of Te by Se atoms leads to the stabilization of the cubic crystal structure of alloys. SEM observations of samples fracture showed changes from the Widmanstätten-type into glass-like microstructure for AgSbTe₂ and AgSbSe₂, respectively. The electrical conductivity, thermal conductivity and Seebeck coefficient were measured as a function of temperature in the range from 300 to 520 K. Electrical conductivity has semiconductor properties within the homogeneous region and semimetallic for the rest of samples. The thermal conductivity is very low as it is in the case of phonon glasses and increases only slightly with temperature. Samples in the homogeneous region have very high positive Seebeck coefficient of about 400-600 $\mu\text{V}\cdot\text{K}^{-1}$ at RT which gives us the opportunity for optimal doping. The ZT parameter describing usefulness of thermoelectric materials, is about 0.65 for the undoped AgSbSe_{0.25}Te_{1.75} sample at a temperature of 520 K.

Keywords: Thermoelectric materials, Electrical properties, Thermal properties, Microstructure, AgSbTe₂, AgSbSe₂

STRUKTURALNE I TERMOELEKTRYCZNE WŁAŚCIWOŚCI UKŁADU AgSbSe₂-AgSbTe₂

Wykorzystując technikę bezpośredniego topienia zsyntezowano dziewięć związków o nominalnych składach AgSbSe_xTe_{2-x} ($x = 0.00, 0.25, \dots, 2.00$). Analiza termiczna i dyfrakcja promieniowania rentgenowskiego ujawniły częściowe podstawienie atomów Te przez atomy Se, prowadzące do stabilizacji regularnej struktury krystalograficznej stopów. Obserwacje SEM przełomów próbek pokazały zmianę ich mikrostruktury od typu Widmanstättena dla AgSbTe₂ do mikrostruktury podobnej do materiału szklistego w przypadku AgSbSe₂. Przewodność elektryczną, przewodność cieplną oraz współczynnik Seebecka zmierzono w funkcji temperatury w przedziale od 300 do 520 K. Przewodność elektryczna ma cechy półprzewodnikowe w obszarze jednorodnym i półmetaliczne w przypadku pozostałych próbek. Przewodność cieplna jest bardzo mała, jak w przypadku szkielec fononowych i zwiększa się tylko nieznacznie wraz z temperaturą. Próbki w obszarze jednorodnym mają bardzo duży dodatni współczynnik Seebecka o wartościach ok. 400-600 $\mu\text{V}\cdot\text{K}^{-1}$ w temperaturze pokojowej, co daje możliwość optymalnego domieszkowania. Parametr ZT opisujący użyteczność materiałów termoelektrycznych ma wartość około 0.65 w przypadku niedomieszkowanej próbki AgSbSe_{0.25}Te_{1.75} w temperaturze 520 K.

Słowa kluczowe: materiał termoelektryczny, właściwości elektryczne, właściwości cieplne, mikrostruktura, AgSbTe₂, AgSbSe₂

1. Introduction

Known as narrow-gap semiconductors the ternary chalcogenides AgSbTe₂ and AgSbSe₂ feature very interesting optical and electronic properties. Both isostructural compounds crystallize in disordered NaCl cubic structure (e.g., Fm3m) in which Ag and Sb randomly occupy the same crystallographic sublattice [1-3]. AgSbSe₂-based alloys are attractive as a switching medium for optical memories because of high reflectance which changes during a reversible amorphous to crystalline-state transition. Considerable changes in resistivity during this transition cause that these materials are considered to be the future non-volatile electronic memories (i.e. PC-RAM). Furthermore, this transition follows small volume changes which do not generate distortion in the material [4-8]. The cubic AgSbTe₂ is a very promising p -type thermoelectric material for the thermal energy conversion at the 500-800 K temperature range. This compound is also

a critical constituent of two classes of high-performance thermoelectric materials, (AgSbTe₂)_{1-x}(GeTe)_x (also called TAGS) and (AgSbTe₂)_{1-x}(PbTe)_x (also called LAST) [9, 10]. However, TAGS and LAST materials have complex microstructures, therefore a better understanding of AgSbTe₂ is needed.

The effectiveness of thermoelectric materials for energy conversion is usually assessed by their dimensionless thermoelectric figure of merit ZT ,

$$ZT = \alpha^2 \sigma \lambda^{-1} T \quad (1)$$

where T is the temperature, α is the Seebeck coefficient, λ is the thermal conductivity, and σ is the electrical conductivity of a material. TAGS, with the maximum value of $ZT_{\text{max}} = 1.5$ at 750 K were considered the best TE materials for quite a long time [9]. The recently discovered LAST with $ZT_{\text{max}} = 2.2$ at 800 K shows the highest noticed figure of merit for bulk thermoelectric materials [10]. However, the applica-

tion of these alloys seems to be limited since due to their thermodynamic instability and inhomogeneity they lose their excellent thermoelectric properties during a long-term annealing at high temperatures. The complicated behaviour of AgSbTe₂-based materials can result from the complex nature of this compound. It has been noticed by many authors that single-crystalline and polycrystalline samples of AgSbTe₂, both prepared in standard conditions [11-15] as well as at high pressure, [16] have small amounts of precipitations of Ab₂Te₃, Ag₂Te, and other phases.

Thermal-analysis investigations of stoichiometric AgSbTe₂ indicate that it does not melt congruently [11-14]. From a pseudobinary phase diagram shown in Ref. [17] one can conclude that the stoichiometric cubic AgSbTe₂ compound existing at high temperature is unstable and decomposes below 655 K to Ag₂Te and Sb₂Te₃. However, it was not confirmed by further investigations of other authors. Extended elaborations of Sb₂Te₃-Ag₂Te and Sb₂Te₃-Ag₂Te-Te phase diagrams confirm that the thermodynamically stable compound with stoichiometric composition of AgSbTe₂ does not actually exist [11-15]. Marin-Ayral *et al.* [14] showed that in the temperature range from 300 to 817 K, the closest stable phase β of a cubic AgSbTe₂ structure has a real chemical composition of Ag₁₉Sb₂₉Te₅₂. This phase displays the behaviour of a solid solution with a narrow homogeneity range coming to 42-44 at.% of Ag₂Te.

AgSbSe₂ seems to have the stoichiometric composition and does not exhibit visible first-order phase transitions up to the melting point at 883 K. It also demonstrates very promising properties, such as large Seebeck coefficient and extremely low thermal conductivity [18].

We expected that the alloying of AgSbTe₂ with isoelectronic and isostructural AgSbSe₂ would allow us to stabilize its structure and obtain homogeneous alloys in some range of compositions. We assumed that the obtained materials should inherit good thermoelectric properties from both base compounds. Therefore the specific objectives of our experimental investigation are as follows: (i) analysing the phase stability in AgSbTe₂-AgSbSe₂ pseudobinary system, (ii) measuring the transport properties of the obtained materials, and (iii) calculating of the thermoelectric figure of merit ZT_{\max} for the obtained alloys.

2. Experimental

We have prepared nine sets of samples with nominal composition of AgSbSe_xTe_{2+x} with $x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75$ and 2.00 . The elements with purity of 99.99 %, in form of small pieces, were closed in sealed quartz ampoules, covered inside with a thin layer of pyrolytical carbon. A synthesis was carried out for 1h at temperature of 700°C in a rocking furnace. At this temperature the elements Te, Se and Sb were melted and Ag was completely dissolved in the melt. After the synthesis ampoules were slowly cooled down to room temperature (RT). The materials were ground and formed in cylindrical samples with a diameter of $d = 10$ mm by using hot-pressing method (graphite dies, argon atmosphere, $T_{\max} = 410^{\circ}\text{C}$, $t = 15\text{min}$, and $p = 30$ MPa). During cooling to RT the pressure was taken off. The samples were cut with a diamond saw and polished. For structural investigations two series of samples were prepared: (i) slowly

cooled down with the rate of 1Kmin^{-1} , and (ii) rapidly cooled down with a rate $> 500\text{Kmin}^{-1}$. For electrical measurement the samples of the cylindrical shape of 15 mm in height and 100 mm in diameter were used. The materials were characterized by X-ray diffraction (X'Pert Philips diffractometer with filtered CuK α radiation) and scanning microscopy (JEOL JSM-840) with the electron-probe microanalysis apparatus. The lattice parameters were determined from the X-ray patterns by the Rietveld refinement method. The thermal analysis of materials was performed by applying a differential scanning calorimeter DSC (TAInstruments DSC 2010). Mass densities were determined with the use of the immersion technique with water as a liquid. Thermal conductivity was measured by two methods: laserflash (Netzsch LFA 457), and the axial heat-flow method in which a specifically calibrated heat-flux sensor designed for measurements of very low thermal conductivities was applied.

3. Results and discussion

3.1. Structural and thermal analysis

Microstructure and phase composition of all AgSbSe_xTe_{2+x} samples were characterized by using X-ray diffraction (XRD), scanning electron microscopy, and DSC techniques. The X-ray diffraction analysis in Fig. 1 revealed that materials with composition parameter $0 \leq x < 1$ consist of the main phase with a cubic structure and a few other phases of which some were identified to be isostructural with Ag₂Te, Sb₂Te₃ and Ag₅Te₃. The amount of precipitations increases during annealing of materials at the temperature of about 600 K and during slow lowering of temperature after their synthesis.

For comparison, Fig. 1 shows the selected results of XRD investigations for slowly cooled samples (series 1) and rapidly cooled AgSbTe₂ material (series 2). It can be noticed that in the case of rapidly cooled AgSbTe₂ the amount of precipitations is practically invisible (less than 2 %). Yet the amount of inclusions in the same material as well as in the samples with composition $0 \leq x < 1$ greatly increase as a result of annealing.

Microscopic investigations presented in Fig. 2a show the Widmanstätten-type microstructure of these samples with

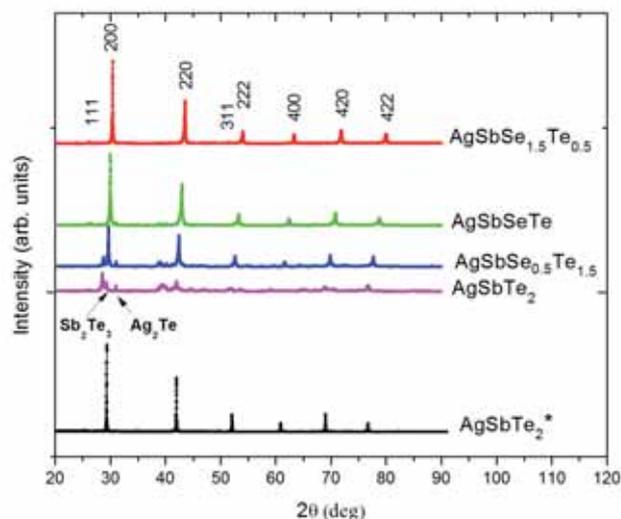
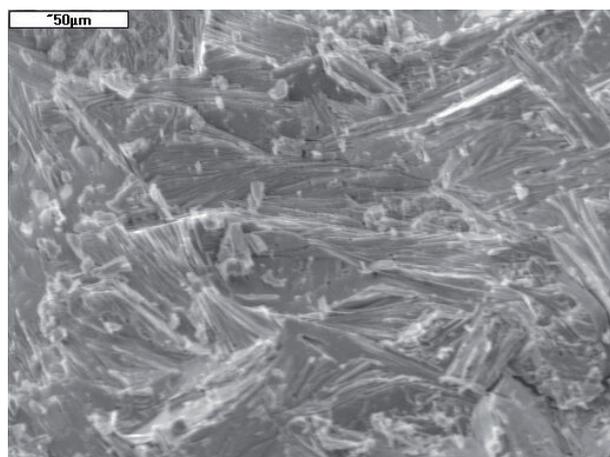
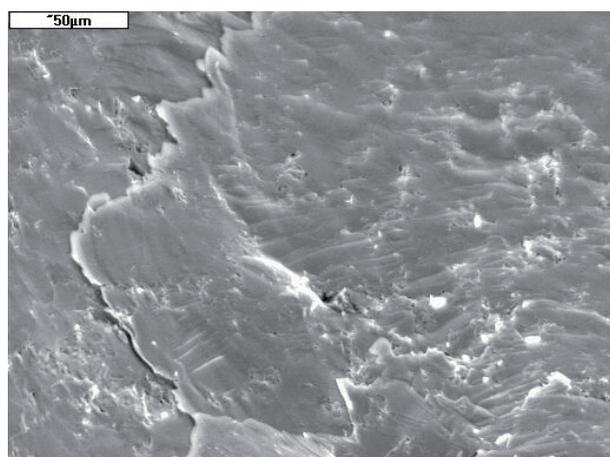


Fig. 1. XRD patterns of AgSbSe_xTe_{2+x} samples (series 1). For comparison, XRD patterns of slowly and rapidly (marked with *) cooled AgSbTe₂ samples are presented.



a)



b)

Fig. 2. SEM picture of the fracture surfaces: a) AgSbTe_2 sample, and b) AgSbSe_2 sample.

visible plate-shape precipitations noticed by others [12, 14]. Fig. 2b shows a glass-like texture for AgSbSe_2 without visible grain borders. The measured density was found to be 98 % of the theoretical value.

The DSC analysis of a sample with the nominal composition of AgSbTe_2 , shown in Fig. 3, reveals the presence of a sharp endothermic peak with broad asymmetrical shoulders which suggests a multifaceted character of phase transitions. The beginning of this peak is situated at the temperature of about 630 K. Therefore, it can be assigned to the melting point of eutectic with a nominal composition of $\text{Ag}_{0.35}\text{Sb}_{0.09}\text{Te}_{0.56}$ (633 K), as given in the ternary phase diagram of Ag-Sb-Te system [14].

The temperature of peak maximum, T_{max} , moves to lower temperatures as a result of alloying with AgSbSe_2 for the subsequent samples with the x parameter changing from 0 to 1 (Fig. 3). For the samples with $x \geq 1$, the endothermic peak vanishes completely. The XRD analysis of the same samples shows no presence of any secondary phases (Fig. 1). Therefore, on the basis of the above observations, we conclude that samples with the composition changing from AgSbTe_2 to AgSbSe_2 ($0 \leq x < 1$) are multi-phased and the samples with the amount of Se larger than Te are homogeneous solid solutions.

The above result is consistent with the observed relationship between cell size, a , and composition parameter,

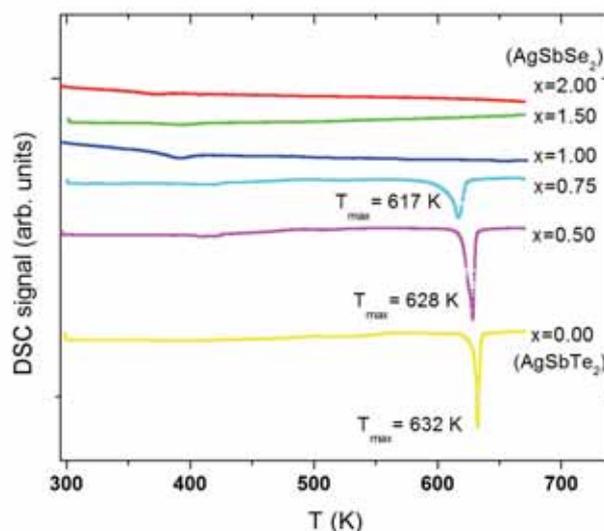


Fig. 3. DSC curves of $\text{AgSbSe}_x\text{Te}_{2-x}$ samples; a heating rate of 5 deg-min⁻¹ and sample masses ranging from 20 to 60 mg were applied.

x , for the main cubic phase of the materials (Fig. 4). The statistical analysis (the parallelism test at a significance level $p = 0.05$) confirmed the presence of two regions with almost linear compositional dependences of cell size. Particularly, it should be noted that Vegard's law is very well carried out for the homogeneous solid solutions. We have expected that the materials in the area of homogeneity should have repeatable properties hence our successive investigations of physical properties were mostly focused on these samples.

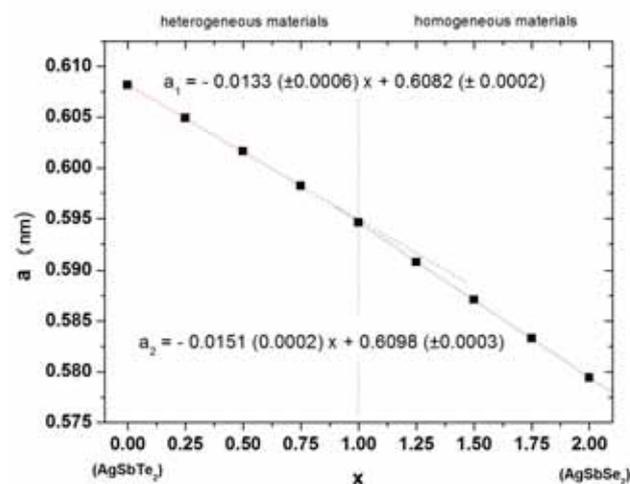


Fig. 4. Lattice parameter a vs. composition x of $\text{AgSbSe}_x\text{Te}_{2-x}$ samples; estimated errors of regression-line coefficients are calculated at the significance level $p = 0.05$.

3.2. Transport properties

Transport properties of the obtained materials, both electrical and thermal conductivities as well as thermopower, are related to their microstructure. Fig. 5 presents selected results of electrical conductivity measurements at 336, 407 and 507 K against chemical composition x . The highest conductance $\sigma = 3.3 \times 10^4 \text{ S} \cdot \text{m}^{-1}$ at RT exhibits the sample with the nominal AgSbTe_2 composition, which is comparable

to the value of $1.5 \times 10^4 \text{ S}\cdot\text{m}^{-1}$ reported for single crystals [19]. Generally, the samples with precipitations of secondary phases exhibit much higher electrical conductivity than homogeneous materials and a semimetallic or metallic behaviour. The single-phased ones ($x \geq 1$) demonstrate semiconducting temperature dependence of electrical conductivity.

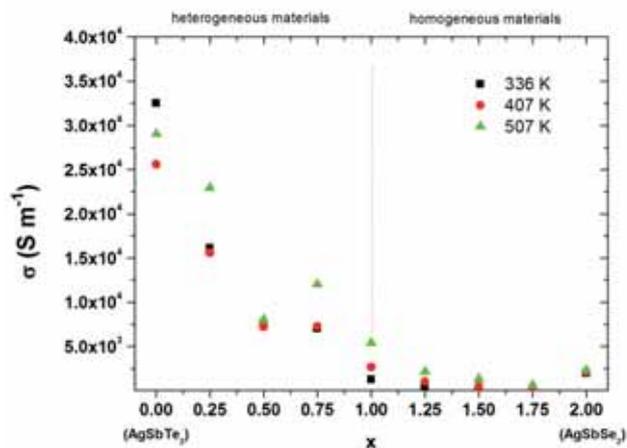


Fig. 5. Variation in electrical conductivity σ with composition x of $\text{AgSbSe}_x\text{Te}_{2-x}$ materials at the temperatures of 336, 407, and 507 K.

Seebeck coefficient measurements were taken for all samples at temperature between 300 and 530 K. Thermopower measurements show that all the samples exhibit a resultant p -type sign of current carriers in the whole temperature range. $\text{AgSbSe}_x\text{Te}_{2-x}$ materials with compositions parameter $x \geq 1$ have very high Seebeck coefficient α of about two to five times higher than the value for pure samples AgSbSe_2 and AgSbTe_2 , respectively. The Seebeck coefficient of heterogeneous samples is lower than single-phased alloys (Fig. 6). All the samples produced, both homogeneous and heterogeneous, are dominantly p -type, which can be due to the presence to Ag vacancies [14], or in the case of inhomogeneous samples, mostly due to microstructural defects and precipitations.

Fig. 7 displays temperature dependences of electrical conductivity in the Arrhenius plot. It can be observed that the base materials AgSbSe_2 and AgSbTe_2 have properties of narrow-band semiconductors. Estimated E_g values for

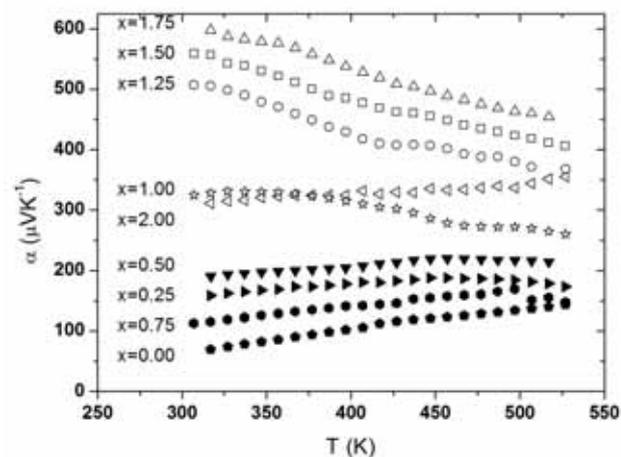


Fig. 6. Temperature dependence of the Seebeck coefficient of $\text{AgSbSe}_x\text{Te}_{2-x}$; filled and hollow markers are related to heterogeneous and homogeneous materials, respectively.

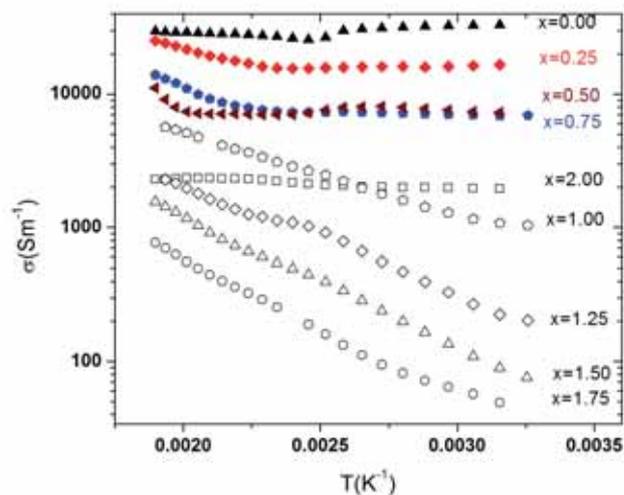


Fig. 7. Temperature dependence of electrical conductivity of $\text{AgSbSe}_x\text{Te}_{2-x}$; filled and hollow markers are related to heterogeneous and homogeneous materials, respectively.

these samples are about 0.09 and 0.03 eV, respectively. This result is consistent with previous measurements and with the results of band-structure calculations for both isostructural compounds, pointing even at their semimetallic features [18, 20]. Interestingly enough, in the case of homogeneous alloys ($x \geq 1$), temperature dependences of electrical conductivity indicate on their apparent thermally activated character ($E_g = \sim 0.3/0.4 \text{ eV}$) in the entire temperature range or, partially, in the high-temperature region ($T > 450 \text{ K}$) for the samples with smaller Se contents ($x < 1$). The evident semiconducting behaviour of homogeneous materials ($x \geq 1$) is correlated with their very high thermopower values, which supports the above observations.

Semiconducting properties of the materials, obtained as a result of alloying of semimetallic AgSbSe_2 and AgSbTe_2 compounds, seem to be an unexpected outcome and cannot be explained as a simple consequence of substitution of Te by isoelectronic Se atoms. We believe that the occurrence of semiconducting properties indicates rather structural changes (e.g., ordering in at least one of sublattices) as a result of alloying and thus subsequent changes in the electronic structure. This supposition is supported by our previous theoretical predictions pointing to a possibility of opening of a band gap in the order AgSbSe_2 (e.g., $\text{Fd}3\text{m}$) [18] as well as by the results of Hoang *et al.* [20] who showed a significant impact of the Ag or Sb ordering on the electronic structure of ternary chalcogenides in the neighbourhood of E_f . However, in order to clarify this problem, more advanced structural investigations are necessary.

3.3. Thermal conductivity

Thermal-conductivity measurements of the samples were performed with the use of two techniques: a precise steady state heat-flow technique which was applied at room temperature and a pulsed laser-flash method for measurements in the temperature scope of 80–600 K. Within the limit of their accuracy both methods provided consistent experimental results.

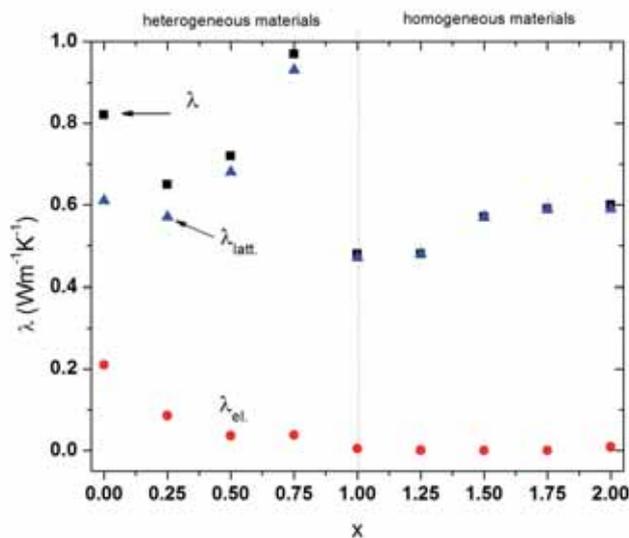


Fig. 8. Variation in thermal conductivities λ , λ_{latt} and λ_{el} with composition x of $\text{AgSbSe}_x\text{Te}_{2-x}$ materials at RT (experimental error 5 %).

Similarly to the results for electrical-transport properties, there are noticeable differences in properties of homogeneous and heterogeneous materials (Fig. 8). Thermal conductivity values of single-phased solid solutions are generally more consistent and lower than for the heterogeneous samples. The discrepancies are visible in particular for base compounds: AgSbSe_2 and AgSbTe_2 . Thermal conductivity λ of AgSbSe_2 is about $0.6 \text{ Wm}^{-1}\text{K}^{-1}$ and is comparable with previous findings, [21] however, thermal conductivity of AgSbTe_2 ($0.82 \text{ Wm}^{-1}\text{K}^{-1}$) is significantly higher than the values reported for single-crystalline $\text{Ag}_{19}\text{Sb}_{29}\text{Te}_{52}$ samples ($0.61 \text{ Wm}^{-1}\text{K}^{-1}$) [19]. This difference as well as generally higher conductivities of heterogeneous materials in comparison with the remaining samples can be the effect of a larger electronic contribution of thermal conductivity λ_{el} , caused by a higher concentration of current carriers generated by, e.g., point defects and inclusions of secondary phases.

The impact of the electronic contribution on thermal conductivity of materials, using Wiedemann-Franz-Lorenz law, was presented in our previous investigation [22].

3.4. Estimation of ZT parameter

The obtained experimental data allow the authors to calculate the dimensionless thermoelectric figure of merit ZT for our materials. Using Eq. (1) we have determined the temperature dependence of ZT parameter. Fig. 8 presents the results for selected materials.

The highest experimental figure of merit $ZT = 0.65$ is possessed by the sample with composition of $\text{AgSbSe}_{0.25}\text{Te}_{1.75}$ at the temperature of 520 K. It can be noticed that, in general, single-phased solid solutions exhibit lower ZT values than the heterogeneous samples, despite their very high Seebeck coefficient α and low thermal conductivity λ . Relatively low ZT values are the consequence of too low electrical conductivity σ resulting from nonoptimal concentration of current carriers in these materials. Further calculations including estimations of optimal ZT value are presented in previous investigation [22].

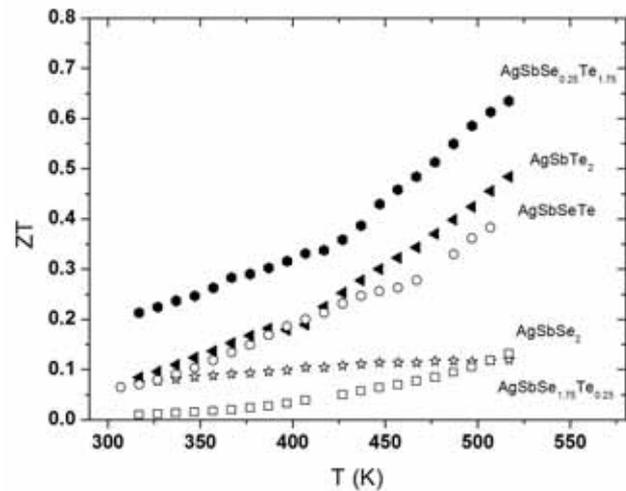


Fig. 10. Temperature dependence of the thermoelectric figure of merit ZT of selected samples; filled and hollow markers are related to heterogeneous and homogeneous materials, respectively.

4. Conclusions

The structural and transport properties in AgSbTe_2 - AgSbSe_2 system from RT to 520 K were studied. The samples with predominant amount of AgSbTe_2 have heterogeneous composition. The remaining materials with excess of AgSbSe_2 are single-phased solid solutions of stable NaCl crystal structure in the wide temperature range. All the samples are p type. Homogeneous alloys of AgSbTe_2 - AgSbSe_2 exhibit apparent semiconducting behaviour ($E_g = \sim 0.3/0.4 \text{ eV}$) in contrary to base compounds and heterogeneous materials which seem to have a much narrower band-gap or semimetallic properties. The band-gap width E_g in homogeneous alloys strongly depends on chemical composition, so a manipulation of Te/Se ratio contributes to tuning the parameter to the required value. Despite that, thermal conductivity of AgSbTe_2 is close to the minimal theoretical value λ_{min} , alloying with AgSbSe_2 leads to a further decrease in heat conduction to $0.48 \text{ Wm}^{-1}\text{K}^{-1}$.

The received materials exhibit very promising initial thermoelectric properties. The highest experimental value of ZT is about 0.65 at temperature of 520 K for the sample with nominal composition of $\text{AgSbSe}_{0.25}\text{Te}_{1.75}$.

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