Thermoelectric properties of $(CuInSe_2)_{1-x}(In_2Te_3)_x$ solid solutions

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Received September 19, 2021
Revised September 24, 2021
Accepted September 24, 2021

The results of studying the temperature dependences of electrical conductivity, thermoelectric coefficient, Hall mobility of charge carriers, total and electronic thermal conductivity, as well as the phonon thermal resistance of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$, where $x = 0.005$ and 0.0075. The values of these parameters for certain temperatures were used to calculate the values of the thermoelectric figure of merit of the indicated compositions. It turned out that with an increase in temperature, the thermoelectric figure of merit tends to grow strongly, which is why it can be concluded that these materials can be used in the manufacture of thermoelements.

Keywords: solid solutions, scattering mechanisms, three-phonon processes, thermoelectric efficiency.

DOI: 10.21883/SC.2022.01.53014.25

1. Introduction

During studying the nature of phase formation in $CuInSe_2$-In_2Te_3 system we observed an area of solid solutions based on compound of $CuInSe_2$ [1]. Compound of $CuInSe_2$, along with prospectivity of application in solar converters, also has clear-cut thermoelectric properties. Considering this feature, under this study we measured temperature dependencies of electrical conductivity, coefficient of thermal EMF, Hall mobility of charge carriers, total and electronic thermal conductivity, as well as phonon thermal resistance of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$ with values of $x = 0.005$ and 0.0075.

2. Experimental procedure

Solid solutions alloys were produced from pre-synthesized polycrystals of $CuInSe_2$ and In_2Te_3, taken in the corresponding ratios. Synthesis was performed in evacuated quartz vessels with vibration mixing of melting at temperature of ~ 1300 K and following slow cooling to room temperature. The resulting compositions were subject to homogenizing annealing for ~ 240 h at temperature of ~ 773 K. Samples quality was controlled with X-ray and microstructure analyses.

Measurements were performed on polycrystal samples within temperature range of 300–800 K as per technique presented in studies [2,3].

3. Results and discussion

Figure 1 shows temperature dependence of electrical conductivity of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$ with 0.5 mol% In_2Te_3 and 0.75 mol% In_2Te_3. As seen, electrical conductivity behavior of both compositions has semiconductor nature with wide area of impurity conduction. Starting from ~ 553 K the intrinsic region is observed. In this region the values of thermal width of forbidden band are calculated for individual compositions of examined samples as per tangent of angle of electric conduction curves.

Figure 1 (see insert) includes the graph of variation of forbidden band width with composition. It was observed that adding of In_2Te_3 into $CuInSe_2$ is accompanied with

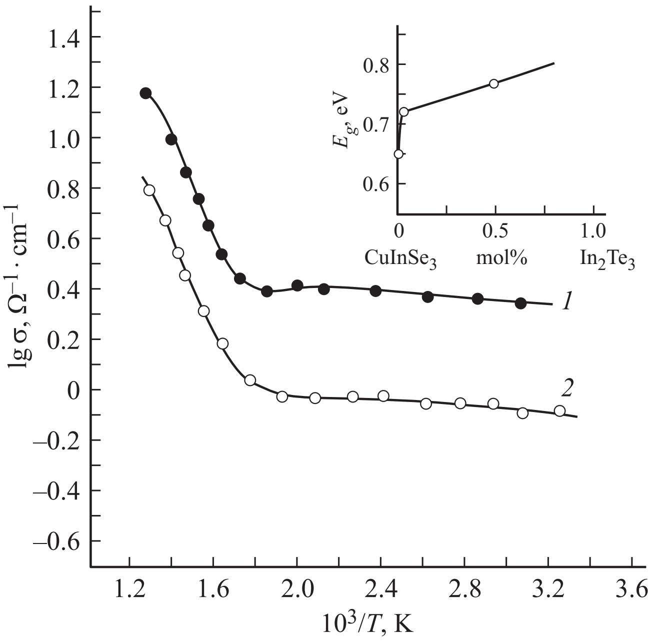

Figure 1. Temperature dependence of electrical conductivity of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$ and variation of value of thermal width of forbidden band depending on composition of these solid solutions (insert): *1* — 0.5 mol% In_2Te_3, *2* — 0.75 mol% In_2Te_3.

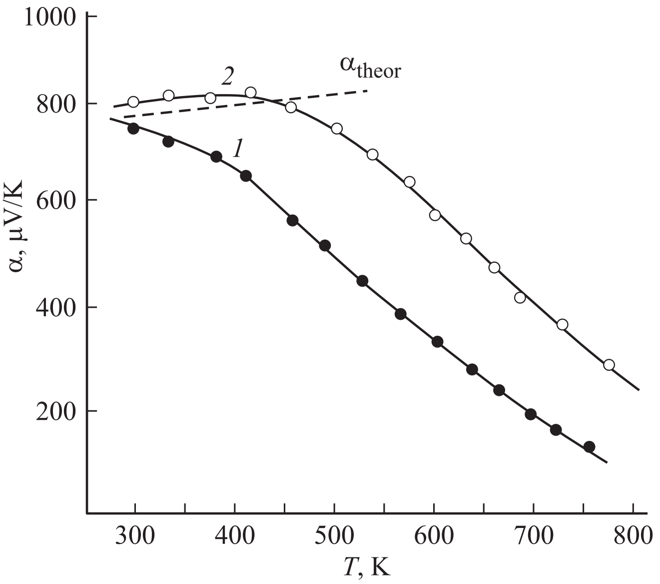

Figure 2. Temperature dependence of coefficient of thermal EMF of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$: *1* — 0.5 mol% InTe, *2* — 0.75 mol% In_2Te_3.

increase of forbidden band width value. Growth of ΔE in examined solid solutions can be explained, considering principles presented in study [4] and similar in study [5]. However, in simple case it is reasonable to note that the added component (In_2Te_3) has the much higher conductivity than the base one $(CuInSe_2)$.

Figure 2 shows the temperature dependence of coefficient of thermal EMF of alloys of examined solid solutions. With temperature increase in the alloy with composition of 0.75 mol% In_2Te_3 to temperature of ~ 450 K the small straight growth of thermal EMF is observed, that is mainly characteristic for multizone semiconductors [6] and qualitatively agreed with theoretical calculations (α_{theor}). Then for this composition and composition of 0.5 mol% In_2Te_3 the coefficient of thermal EMF reduces. However it should be noted that with increase of In_2Te_3 content in the composition the thermal EMF takes higher values in absolute terms.

Figure 3 shows temperature dependencies of Hall mobility of charge carriers of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$. Below temperature of ~ 540 K the Hall mobility of charge carriers shows tendency to growth and, passing through flat maximum, decreases under higher temperatures. It was observed that below ~ 540 K Hall mobility complies with the law $T^{3.5}$. The reason for high value of scattering degree can be multi-zone nature of energy spectrum, as evidenced by Fig. 2. Above temperature of maximum on $\lg U_H \sim f(\lg T)$ curves the reduction of mobility is observed, where the law $T^{-3.5}$ and charge carriers scattering from thermal vibrations of crystal lattice prevail. High absolute values of degree indicate the presence of additional mechanisms of charge carriers scattering in the examined samples. It seems that with temperature increase the contribution of conductivity band to electrons Hall effect becomes significant.

Since examined alloys are polycrystalline, they are characterized with high degree of disorder and presence of additional scattering centers. There is a good probability that beside that the appearance of additional scattering centers of charge carriers can be resulted by presence of tellurium atoms in alloys composition, since tellurium impurities can create such scattering centers in semiconductor materials [7].

Figure 4 shows temperature dependencies of total thermal conductivity of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$. As seen, with temperature increase the gradual decrease of thermal conductivity is observed, indicating the prevalence of three-phonon scattering processes in the examined solid solutions.

Calculations have shown that variation of total thermal conductivity with temperature is subject to law $\sim T^{-0.1}$.

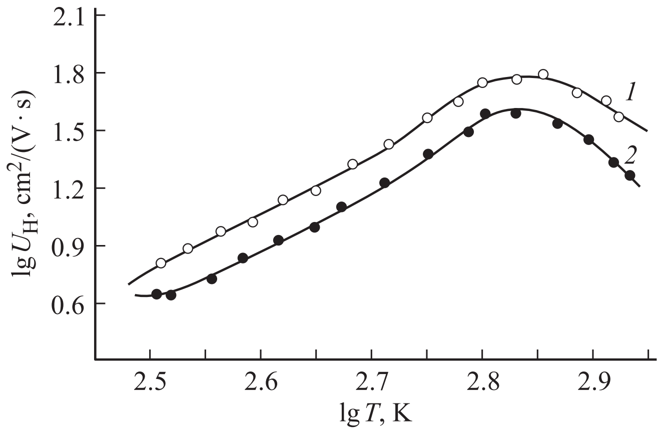

Figure 3. Temperature dependence of Hall mobility of charge carriers of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$: *1* — 0.5 mol% In_2Te_3, *2* — 0.75 mol% In_2Te_3.

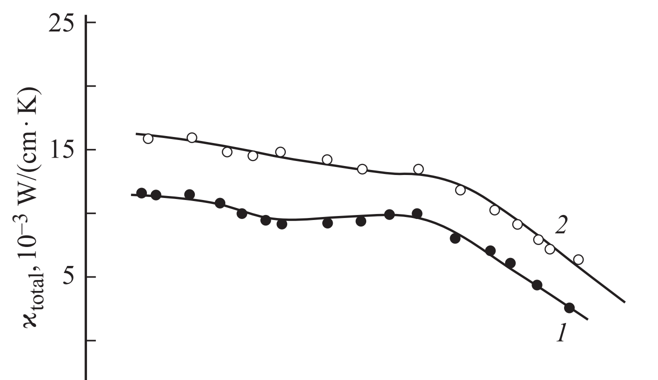

Figure 4. Temperature dependence of total thermal conductivity of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$: *1* — 0.5 mol% In_2Te_3, *2* — 0.75 mol% In_2Te_3.

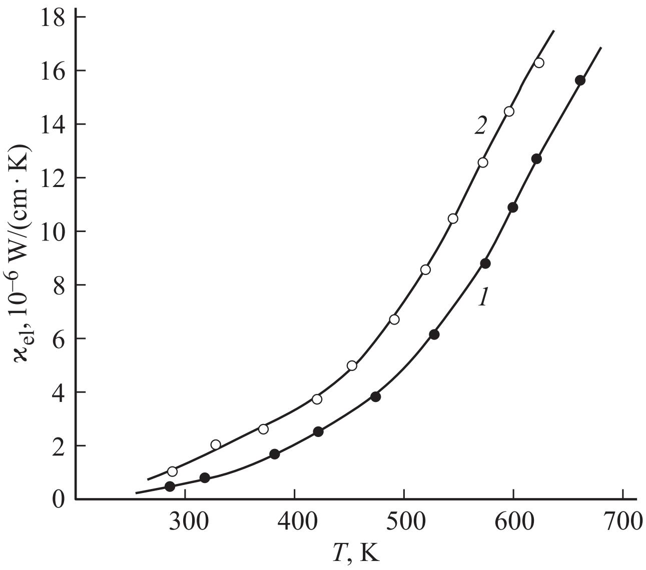

Figure 5. Temperature dependence of electronic conductivity of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$: *1* — 0.5 mol% In_2Te_3, *2* — 0.75 mol% In_2Te_3.

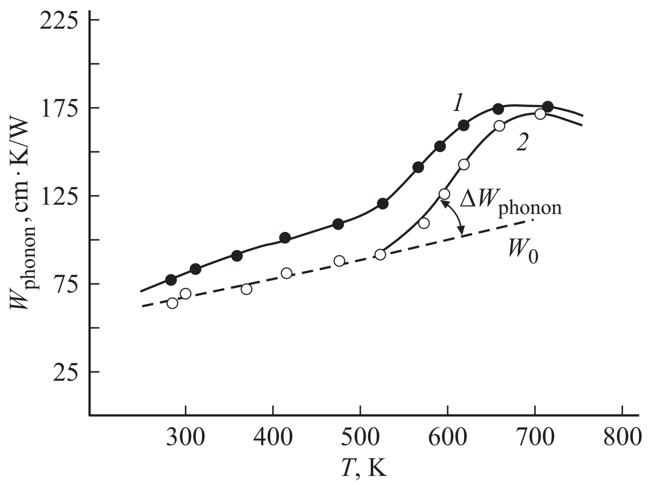

Figure 6. Temperature dependence of phonon thermal resistance of alloys of solid solutions $(CuInSe_2)_{1-x}(In_2Te_3)_x$: *1* — 0.5 mol% In_2Te_3, *2* — 0.75 mol% In_2Te_3.

Using Wiedemann–Franz formula [8] the shares of electronic thermal conductivity are calculated and their temperature dependencies are built (Fig. 5). It was observed that with temperature increase $æ_{el}$ strongly increases, but this increase does not significantly contribute to decreasing total thermal conductivity, since quantitative value of electronic thermal conductivity is small ($\sim 10^{-6}$ W/(cm · K)).

Considering that bipolar and photon thermal conductivity are negligible (under high temperatures there is no increase of total thermal conductivity and measured samples are nontransparent), the values of phonon component of thermal conductivity are calculated using the difference of $æ_{ph} = æ_{total} - æ_{el}$. Values of phonon thermal resistance are defined from ratio $1/æ_{ph}$ for various temperatures. Temperature dependence of this parameter for both examined solid solutions is presented in Fig. 6.

Below temperature of ~ 550 K the variation of W_{ph} is straight, that qualitatively agrees with theoretical values of this parameter. However, starting with ~ 550 K the variation of phonon thermal resistance becomes stronger, that indicated the appearance of additional phonon thermal resistance (ΔW_{ph}). Variation of phonon thermal resistance with temperature indicates to the three-phonon scattering mechanism in the examined compositions of alloys. Increase of values of degree coefficient in temperature dependence of thermal resistance indicates to the additional mechanisms of heat transfer [8]. Such complexity of heat transfer can be related to multi-component nature and defectiveness of composition of the examined alloys [9,10].

Values of thermoelectric figure of merit of solid solution with 0.75 mol% In_2Te_3 were calculated using the general formula $Z = \alpha^2\sigma/æ_{total}$. It was observed that at 300 K this composition has $Z = 0.15 \cdot 10^{-3}\,\text{degr}^{-1}$, and at 700 K $Z = 0.52 \cdot 10^{-3}\,\text{degr}^{-1}$. Despite the small values of thermoelectric figure of merit they can be considered as acceptable for the technique of thermoelectric energy conversion.

4. Conclusion

Thus, according to the results of this study, we can conclude that along with the fact that $CuInSe_2$ compound and alloys based on it are reliable materials for solar photovoltaic energetics [11,12], they can be also included in a family of prospective thermoelectric materials.

Conflict of interest

The authors declare that they have no conflict of interest.

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