THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF CHALCOGENIDE GLASS As₂Se₃ FROM ROOM TEMPERATURE TO MELTING POINT

BUDKE, O.,[1] Bratislava

The temperature dependence of thermal conductivity and thermal diffusivity of chalcogenide glass As_2Se_3, pure and doped with In and Ag, was measured on small planparallel samples ($\sim 1.4 \times 5 \times 5$ mm³ and smaller) from room temperature to the melting point by a non-stationary method. The results for thermal conductivity differ remarkably from those obtained by stationary methods and partly from those obtained by other non-stationary methods for various chalcogenide glasses. The heat capacity per unit volume was calculated from the measured values of thermal conductivity and thermal diffusivity. These results are compared with the specific heat, which other authors measured by a different independent method.

1. INTRODUCTION

The temperature dependence of the thermal conductivity of chalcogenide glasses of various compositions is well known today in the range of temperatures from liquid nitrogen temperature T_N up to the melting point T_m and even above this point.

All these results can be divided into two classes: results obtained by means of stationary methods and on the other hand, results obtained by means of non-stationary methods. Let us briefly introduce the main characteristics of these results without pretension to be complete.

The stationary method showed [1, 2, 3] that the thermal conductivity of chalcogenide glasses of various composition increases with temperature from the liquid nitrogen temperature to the transformation region temperature T_g. Thomas and Savage [4] present the thermal conductivity λ of tellurium-based chalcogenide glasses as temperature independent in this temperature interval with $\lambda = $ const. c_V, where c_V is the specific heat at constant volume. For the higher temperatures T, $T_g < T < T_m$, Amirchanov et al. [5—8]

measured a significant increase of λ with a maximum in this interval for various chalcogenide glasses. We stress the point that these measurements have been realized by stationary methods with total measuring time of $15 \div 20$ hours.

Abdulaev et al. [9] measured by a stationary method the thermal conductivity of glassy selenium. It was shown by a stationary method the thermal conductivity of glassy selenium. It was shown that up to $31°C$ the λ-values of pure selenium increase linearly with temperature. At $T = T_g = 31°C$ the value of λ increases suddenly by about 40 %. Qualitatively analogous results were constructed in [10] from the measured values of the thermal diffusivity $k(T)$ and results of the heat capacity $c_p(T)$ and the density $\varrho(T)$ of other authors (loc. cit. in [10]) according to the formula $\lambda = c_p \varrho k$.

In cases when authors interpreted the dependence $\lambda(T)$ for temperatures between T_N and T_g, they usually applied the dominant-phonons approximation and Debye's formula $\lambda = c \cdot v \cdot l/3$ (c — the heat capacity per unit volume, v — the velocity of the dominant phonons and l — their mean free path). At this temperature interval it is supposed that $l \approx$ const., $v \approx$ const. and the increase of the thermal conductivity is ascribed to the increase of the thermal capacity with temperature (interpretation according to Kittel [11]).

The thermal parameters of various chalcogenide glasses were investigated by means of non-stationary methods as well.

Rozov et al. [12] used a dynamical method for the determination of $\lambda(T)$, $T_{room} < T < T_g$, for various compositions of As-Se and As_2Se_3-As_2Te_3 glasses. In all cases thermal conductivity was increasing with temperature.

The dynamical method with a planar pulse heat source proposed by Kulakov [13] enables an independent measurement of thermal conductivity (or the heat capacity per unit volume) and thermal diffusivity. This method has been well elaborated and improved today. Kubičár and Krempaský [14] analyzed it with regard to the influences of thermal losses from the surface of the sample and of thermal resistance of the contact between the heat source and the sample or of an intermediary layer in this contact. Kubičár described an equipment for measuring thermophysical quantities by this method between $20 \div 300°C$ in [15]. An equipment for measuring isothermally and nonisothermally thermophysical quantities in the temperature range of ($-150 \div 1500)°C$ is described in [16]. There is also analyzed the influence of the heat pulse width on the measured values there (in theory the heat pulse is the δ-function).

Doupovec in [17] measured by means of the method [13] the temperature dependence of thermal conductivity and thermal diffusivity of Se and the glassy $Ge_{15}Te_{81}S_2As_2$. Pridalová and Doupovec [18] described the same parameters for the glassy and crystalline $Te_{70}Ge_{10}As_{20}$, which were obtained by the method [13], [14]. In both cases the temperature range included the transformation region, the crystallization region and melting. There were various heating rates used, too.

[1] Katedra fyziky, EF SVŠT, Mlynská dolina, 81219 BRATISLAVA, Czechoslovakia

The relative changes of specific heat per unit volume, thermal diffusivity and thermal conductivity with temperature were studied in [19] in the neighbourhood of the transformation point for glassy specimens of selenium containing from 1 to 20 atomic percent of arsenic.

Finally, the dynamical method with a planar pulse heat source was applied by Illeková and Kubičár [20] to the investigation of the temperature dependences of the heat capacity per unit volume ratio and the thermal diffusivity ratio of powdered glassy and crystalline samples of GeS_x, x from 1.25 to 1.5, at temperatures ranging from room temperature up to melting points.

Trnovcová et al. [21] give three numerical values of thermal diffusivity for the glass As_2Se_3 + 5 mol.% Pb: $k(glass) = 1.3 \times 10^{-7}$ m²/s, $k(liquid) = 9 \times 10^{-8}$ m²/s and $k(cryst) = 2.5 \times 10^{-7}$ m²/s.

All the results obtained in [17—20] cannot be discussed here in detail. Some of them will be compared with our results introduced in chapter 3. Let us tress here only the most important characteristics common to most of the measured materials: Softening an crystalizing are not point phenomena, but in the most investigated chalcogenide glasses they are realized in temperature intervals of some tens of degrees. At the same time the processes of softening and crystallization are influenced by the magnitude and linearity of the heating rate in the sample. The thermophysical parameters (especially thermal diffusivity) detect sensitively the changes of the microstructure of glasses [17—21].

As far as we know the temperature dependence of the thermal conductivity λ at temperatures from the room temperature up to the melting point for the selenium-arsenic glass in the stoichiometric structure of As_2Se_3 has been investigated only by means of stationary methods. The dispersion of the known values of λ at room temperature for As_2Se_3 is considerable. For an illustration we give the values of λ in Table 1. Such a large dispersion of values is difficult

Table 1

The values of the thermal conductivity λ for As_2Se_3 at room temperature given by various authors (modification g — glassy, c — crystalline; the value* obtained by interpolation).

reference	modification	λ [W/mK]
1	g	0.7
2	g	0.63
5	g	0.5
22	g	0.33
3	g	0.25
12	c	0.18*
5	c	1.4
1	c	1.3

to explain only by technological differences in the preparation of samples. As explanation we have to consider foremost the differences of the used method and their adjustments.

2. THE METHOD OF MEASURING AND THE PREPARATION OF SAMPLES

Budke and Dieška elaborated a non-stationary method [23] for an independent measurement of the thermal conductivity λ and the thermal diffusivity k, which is applicable to the relatively small planparallel samples.

The principle of the method consists in measuring the time dependence of the temperature of a plane heat source heated by a constant power (Joule's heating) during a finite time interval. The measured specimens are symmetrically placed round the heat source. It is supposed that the temperature of one of the specimen sides is equal to the temperature of the heat source, the opposite side of the same specimen has the temperature of a furnace (or of the sample holder). These conditions confine the applicability of this method above all to materials with $\lambda \leq 10$ W/mK.

The heat capacity of the source was already taken into account in the formulation of the problem. This last fact and the perfect thermal contact between the thermocouple and the heat source, the temperature of which is to be measured (contact metal—metal), are advantages of this method.

The heat source was a meander of the thickness of 50 μm made of a nickled copper foil. The temperature difference ΔT on the specimen was measured by a differential thermocouple Fe-constantan with the diameters of the wires 50 μm and 40 μm, respectively. The temperature difference ΔT on the specimen was shown to appear some time after the heat impulse had started [23] the function

$\Delta T = A[1 - B \exp(-t/\tau_1)]$, A, B, τ_1 being constants, t — time. Knowing A (practically for $t \gg \tau_1$) and τ_1 one can determine the thermal conductivity and thermal diffusivity, respectively. We have recorded ΔT by means of a Digital Voltmeter Type 2805 fy YEV, Japan, equipped with a millivolt-meter unit Type 2832 (0.1 μV/digit) or recorder Mikrograph BD 5-686 E fy Kipp Zonen, Netherlands. In our experiments ΔT_{max} was about $1.0 \div 1.5°C$, which enabled measuring the dependences $\lambda(T)$ and $k(T)$ in steps of about two degrees.

In [23] a model was also proposed to estimate a parasitical heat flow through the lead-in-wires of the heat source and the wires of the thermocouple used for measuring the temperature of the heat source. Because the heat source was made in the shape of a meander a geometrical correction factor was calculated, too [23].

The errors of measurements are due to the corrections both for λ and k less than 10 %. Our equipment allowed to distinguish reliably the relative change of λ by 2 % measuring on the same specimen. As regards the k-measurements,

there were temperature intervals, in which for given thicknesses of specimens the time constant τ_1 was about $0.6 \div 1$ s, the time near the limit of the possibilities of our equipment. That explains the considerable dispersion of the values $k(T)$ or $c_p\varrho(T)$ (see Fig. 3, curve d) for the smallest of our samples of $As_2Se_3 + 3$ mol. % In (of dimensions $5.06 \times 2.95 \times 0.53$ mm³ only).

By means of the above described method we have measured the thermal conductivity λ and the thermal diffusivity k of the following samples of chalcogenide glasses: pure As_2Se_3 and As_2Se_3 doped with 0.5, 1 and 3 mol. % In and with 1 and 2 at. % Ag, respectively. The first series of samples were processed by the method of a two-level cooling from the melt kept for 10 hours at 850°C. The first stage of the cooling was at $600 \div 650$°C for $1 \div 2$ hours. The material was then put into the furnace at 180°C for 1 hour and further cooled for 5 hours down to room temperature [24]. The technology of the preparation of the samples of As_2Se_3 doped with Ag is not known [25].

The typical sizes of out plane-parallel specimens were: $a = 5$ mm, $b = 5$ mm and the thickness $x_0 = 1 \div 1.4$ mm. Before the measurements of the thermal parameters we had checked each sample by means of X-ray diffraction. The glassy state was confirmed for each specimen.

3. RESULTS AND DISCUSSION

The results of our measurements of the thermal diffusivity k and of the thermal conductivity λ for glassy As_2Se_3 doped with In are in Figs. 1 and 2. In Fig. 3 there are the values of the heat capacity per unit volume $c_p\varrho = \lambda/k$ calculated from the measured values of λ and k. The results for glassy As_2Se_3 doped with Ag are qualitatively the same and are not given in figures — the differences will be mentioned in what follows.

The thermal diffusivity k (Fig. 1) is constant from room temperature up to the transformation region (at about 180°C). This holds for all the specimens of As_2Se_3 doped with In (and Ag, too). In the above mentioned temperature region th thermal conductivity λ grows linearly. The course of the heat capacity per unit volume $c_p\varrho = \lambda/k$ is analogous (c_p — specific heat at constant pressure, ϱ — density) (see Fig. 3). The increase in $\lambda(T)$ in this temperature region was found in papers [1—8], [12], [17] and [20] as well. It would suggest that at this temperature interval the thermal conductivity rises according to the increase of the thermal capacity with temperature [11].

Thermal diffusivity immediately reveals microprocesses in the structure of materials. In the transformation region there appears with increasing temperature a sudden drop in the viscosity of glasses and the values of the elasticity coefficient decrease [26]. The consequence is a drop in the sound velocity in the glasses and the phonon velocity v. Kittinger et al. [27] found that for the

glassy Se the velocity of ultrasonic waves decreases in the interval $10 \div 30$°C, but at $T = T_g = 30$°C it begins to decrease more rapidly. This was confirmed in experiments of E t i e n n e et al. [28].

In the dominant phonons approximation we can write for the thermal diffusivity $k = 1/3 . v . l$. The mean free path of phonons should not be changed substantially for the transformation region and for the state of an undercooled liquid, because the short range order exists at these temperatures. The transition into the liquid state and the decrease of the viscosity in the transformation region are caused not by the destroying of the bonds, but by transformations of the covalent bonds [29]. Thus a drop in the thermal diffusivity should appear during the softening due to a decreased velocity of the phonons.

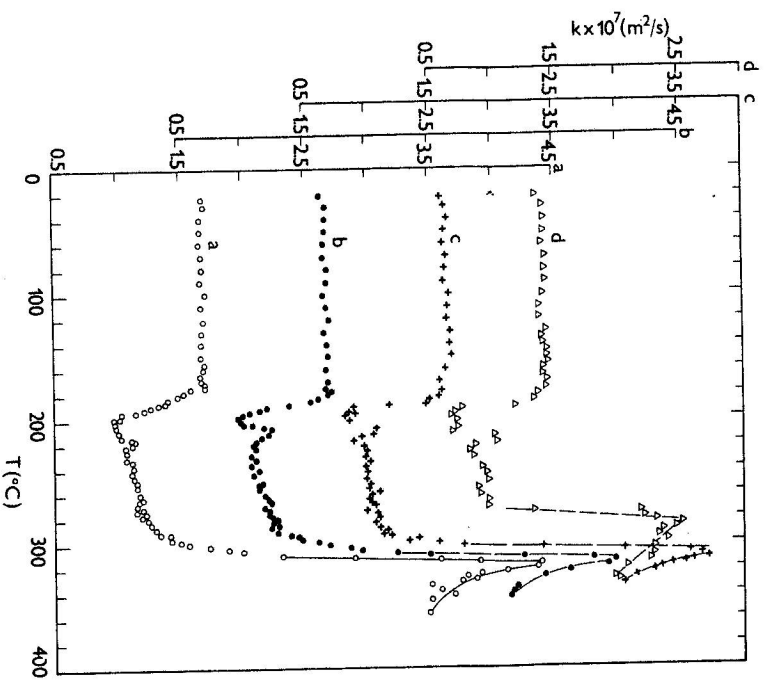From Fig. 1 on can see that in the transformation region k really decreases

$k \times 10^7 \, (\text{m}^2/\text{s})$

$T \, (°C)$

Fig. 1 Temperature dependence of the thermal diffusivity $k(T)$: a — pure As_2Se_3; b, c, d — As_2Se_3 doped with 0.5, 1, 3 mol. % In

and reaches its minimum. This minimum is followed by a slight local maximum shifted by about 20 degrees to the elevated temperatures (this local maximum not observed for As$_2$Se$_3$ doped with Ag).

For the liquid state the values of k are growing slightly quasilinearly with temperature up to the temperature when specimens begin to crystallize. With the gradual crystallition k grows abruptly to two- or threefold values of k at room temperature. In the crystallization temperature region both the mean free path and the velocity of phonons increase because of an ordering and strenghtening of bonds in the crystallized regions. (Such an interpretation of the k growth is supported by the results of measuring λ — see below.)

One of the most interesting results of our measurements are the temperature dependences of the thermal conductivity in the transformation region and about 100 degrees (for As$_2$Se$_3$ with Ag only 70 degrees) above this region. From Fig. 2 a linear growth of $\lambda(T)$ is evident for this temperature interval, without any extraordinary changes or peaks. In the transformation region peaks in $\lambda(T)$ were found for Se [9], [17] and for Te$_{70}$Ge$_{10}$As$_{20}$ [18]. The course of $\lambda(T)$ was
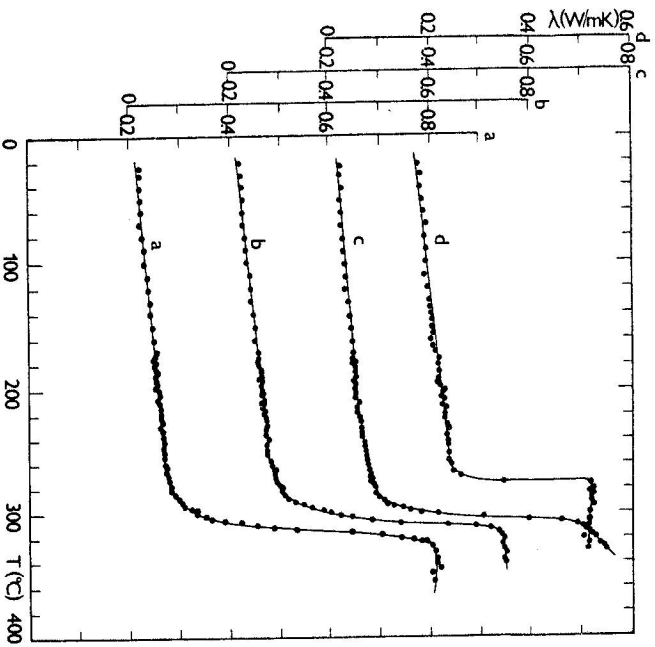

Fig. 2 Temperature dependence of the thermal conductivity $\lambda(T)$: a — pure As$_2$Se$_3$; b, c, d — As$_2$Se$_3$ doped with 0.5, 1, 3 mol. % In

found to be more complicated for Se + x at. % As ($x = 1, 5, 10, 15, 20$) [19], because λ shows a peak up and immediately a peak down (like an oscillation in T). A peak for GeS$_x$ ($x = 1.25 \div 1.5$) could be reconstructed from data in [20] for this region, too.

The significant increase of λ observed for various materials of chalcogenide glasses in [5—8] is of a different character — the increase in $\lambda(T)$ with a maximum take place at tempertures above T_g and the peak is not so sharp. In our opinion the measured samples could be crystallizing during the stationary measurements (see below).

We have also measured a rapid growth of λ, but at remarkably higher temperatures — at about $80 \div 100$ degrees above T_g. We interprete this increase in $\lambda(T)$ as a consequence of continuing crystallization of the specimens. One repeated measurement of $\lambda(T)$ for another glassy and polycrystalline specimen of As$_2$Se$_3$ (Fig. 4) supports such an interpretation. Returning from the temperature $T_{et} = 329°C$ to room temperatures, the values of λ follow the dependence shown in equation $\lambda = \text{const}/T$, typical for crystalline (or polycrystalline) dielectric materials. We repeated the measurement of $\lambda(T)$ of the same sample
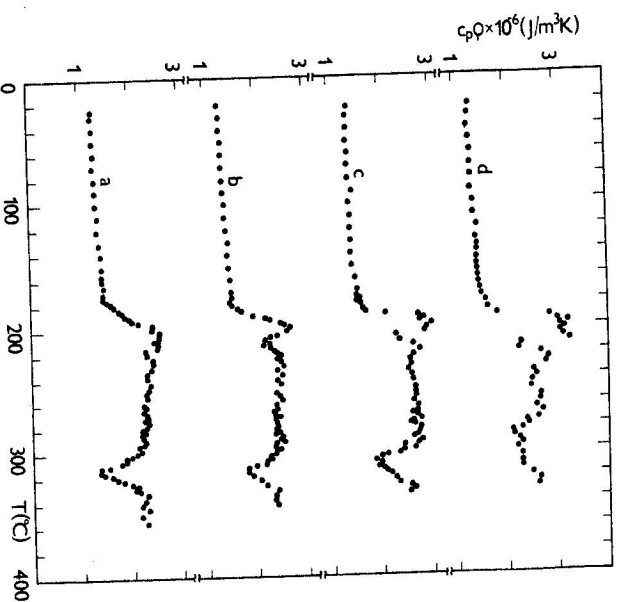

Fig.3 Temperature dependence of the heat capacity per unit volume $c_p\varrho(T)$, calculated from data presented in Figs. 1 and 2: a — pure As$_2$Se$_3$; b, c, d — As$_2$Se$_3$ doped with 0.5, 1, 3 mol. % In
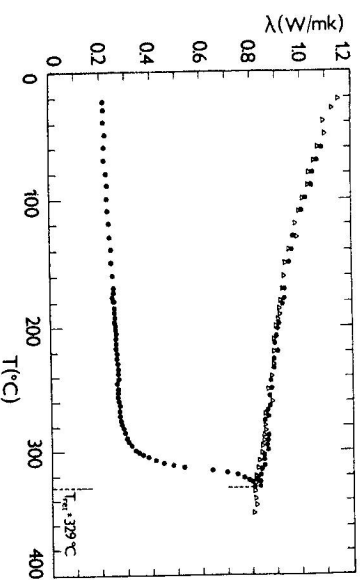
Fig. 4 Temperature dependence of the thermal conductivity $\lambda(T)$ of glassy and polycrystalline As₂Se₃; values (•••) for increasing temperature up to the returning point T_{ret} = 329°C, values (•••) for decreasing temperature from T_{ret} to room temperature, values (△△△) for repeated measurement on the same sample up to the melting point (T_{melt} = 356°C).

from room temperature to the melting point. The values follow precisely the previous dependence and confirm that at the temperature of T_{ret}, the sample was already crystalline. An analogous course for a polycrystalline As₂Se₃ was measured by Kolomiets et al. [1] and Amirchanov et al. [5] by means of stationary methods. In [5] a slight increase of λ took place at temperatures above 230°C up to the melting point.

Looking at Table 1 one can see that our results of thermal conductivity at room temperature fall into the interval of the values measured by other authors and are placed above its bottom (for pure As₂Se₃). The concentration of impurities in an amount of 0.5 and 1 mol. % In has practically no influence upon the thermal conductivity of As₂Se₃, while at 3 mol. % of In a small decrease of the values of λ occurs.

We have also observed that the increase in the impurity of Ag decreases the thermal conductivity: λ (24°C) = 0.195 W/mK for 1 at. % of Ag and 0.17 W/mK for 2 at. % of Ag. A decrease of λ with impurity Ag was found also by Štourač et al. [2]. The impurity Ag decreases the crystallization region of about 30 ÷ 40 degrees down in comparison with the undoped sample.

Today it is generally known that the absolute values of softening and crystallization temperatures are functions of the thermal history of samles or of the heating rates during experiments. For chalcogenide glasses this fact can be seen for example in [17] and [18]. We have used these mean heating rates: for glass and liquid W = 1 K/min., for the transformation and crystallization regions W = 0.34 K/min.

We have to compare yet our calculated function $c_p \varrho(T) = \lambda/k$ with such a function measured by a different and independent method. For example,

Orlova and Muromcev [30] measured the thermal capacity at constant pressure c_p by a calorimetric method (their heating rate W = 0.3 K/min.). If we take into account a mild decrease of the density ϱ with temperature, as observed by Gutenev and Aninitchev [31], we can see that our results for $c_p \varrho$ qualitatively conform with those of c_p in [30] (excepting a little local minimum after the maximum, which follows from the course of k). This comparison concerns the temperature interval from 47°C to 257°C — the values given in [30]. Taking c_p from [30] and ϱ from [31] for temperatures of 127°C (glass) and 257°C (liquid) we calculate $c_p \varrho$ (127°C) = 1.59 J/cm³K and $c_p \varrho$ (257°C) = 2.73 J/cm³ K. Our values at these temperatures are $c_p \varrho$ (127°C) = 1.4 J/cm³ K and $c_p \varrho$ (257°C) = 2.25 J/cm³ K, which makes 88% and 82% from the previous ones.

At the temperature of the most rapid crystallization the values of $c_p \varrho$ reach a local minimum.

4. CONCLUSION

The temperature dependence of the thermal conductivity and of the thermal diffusivity of As₂Se₃ (and doped with 0.5, 1, 3 mol. % In and 1, 2 at. % Ag) from room temperature to the melting point was measured by a non-stationary method [23].

Our measurements show the dependence of thermal conductivity to be slowly linearly increasing for all specimens of As₂Se₃, doped with In from room temperature to the temperature about 100°C above T_g with the slope $\sim 2.5 \times 10^{-4}$ W/mK². Then crystallization of samples takes place and the thermal conductivity rapidly increases towards the values for a polycrystalline material. The increase of the impurity In decreases somewhat the crystallization temperature region and quickens the crystallization.

For the thermal conductivity no anomalies and peaks have been observed at the transformation region.

It has been shown that the results for $c_p \varrho(T)$ are at least qualitatively the same as observed by other authors [30, 31] (with a little exception — the jump in $c_p \varrho$ at T_g goes through a maximum, which is in our case followed by a small narrow minimum) in the interval 47°C ÷ 257°C. The function $k(T)$ shows very sensitively the transformation region, the start and the region of crystallization of the samples.

The results for As₂Se₃ doped with 1 and 2 at. % Ag are qualitatively the same as for this material doped with In.

The method we have used [23] has been shown to be very suitable for measuring the thermal parameters of small, weak conductive samples.

REFERENCES

[1] Kolomiets, B. T., Pajasová, L., Štouráč, L.: Fiz. tverd. tela 7 (1965), 1588

[2] Štouráč, L., Kolomiets, B. T., Šilo, V. P.: Czech. J. Phys. B 18 (1968), 92

[3] Flasck, A., Rockstad, H. K.: J. Non-Cryst. Sol. 12 (1973), 353

[4] Thomas, C. B., Savage, J. A.: J. Non-Cryst. Sol. 23 (1977), 139

[5] Amirchanov, Ch. J., Magomedov, J. B., Ismailov, S. M.: Fiz. tverd. tela 17 (1975), 3628

[6] Amirchanov, Ch. J., Magomedov, J. B., Ismailov, S. M., Alieva, Ch. O.: Fiz. i techn. poluprovodnikov 13 (1979), 595

[7] Amirchanov, Ch. J., Magomedov, J. B., Ajdamirov, M. A., Ajo, L. G., Alieva, Ch. O., Ismailov, S. M.: Fiz. i chimia stekla 6 (1980), 312

[8] Amirchanov, Ch. J., Magomedov, J. B., Ajdamirov, M. A., Alieva, Ch. O., Ismailov, S. M.: Fiz. i chimia stekla 8 (1982), 681

[9] Abdulaev, G. B., Mekhieva, S. I., Abdinov, D. Sh., Aliev, G. M., Alieva, S. G.: Phys. stat. sol. 13 (1966), 315

[10] Orthmann, H. J., Ueberreiter, K.: Kolloid-Zeitsch. 147 (1956), 129

[11] Kittel, Ch.: Phys. Rew. 75 (1949), 972.

[12] Rozov, I. A., Tshudnovskij, A. F., Kokorina, V. F.: Fiz. i techn. poluprovodnikov 1 (1967), 1159

[13] Kulakov, M. B.: Teplo i massoperenos. Izdat. Akad. Nauk BSSR, Minsk 1962.

[14] Kubičár, L., Krempaský, J.: Phys. stat. sol. (a) 2 (1970), 739

[15] Kubičár, L.: Fyz. čas. SAV 22 (1972), 129

[16] Kubičár, L.: Čs. čas. fyz. A 34 (1984), 153

[17] Doupovec, J.: Thesis. Fyzikálny ústav SAV, Bratislava 1972

[18] Pridalová, E., Doupovec, J.: Acta phys. slov. 23 (1973), 224

[19] Králová, B.: Czech. J. Phys. B 22 (1972), 704

[20] Ileková, E., Kubičár, L.: Acta phys. slov. 28 (1978), 292

[21] Trnovcová, V., Ležal, D., Doupovec, J., Mariani, E., Králová, B.: in: Proceedings Amorphus Semiconductors '78, Pardubice 1978, vyd. pobočka ČVTS pri ÚFPL ČSAV Praha 1978, p. 289

[22] Uphoff, H. L., Healy, J. H.: J. Appl. Phys. 32 (1961), 950

[23] Budke, O., Dieška, P.: Acta phys. slov. 35 (1985), 27

[24] Ležal, D.: private communication

[25] Barančok, D.: private communication

[26] The Physics of Glassy Polymers. Ed.: Haward R. N., Applied Science Publishers LTD, London 1973

[27] Kittinger, E.: Phys. stat. sol. (a) 42 (1977), K 33

[28] Etienne, S., Guenin, G., Perez, J.: J. Phys. D 12 (1979), 2189

[29] Nemilov, S. V.: Fiz. i chimia stekla 4 (1978), 662

[30] Orlova, G. M., Muromtsev, V. A.: Fiz. i chimia stekla 5 (1979), 361

[31] Gutenev, M. S., Aninitshev, V. A.: Fiz. i chimia stekla 13 (1987), 346

ТЕПЛОПРОВОДНОСТЬ
И ТЕМПЕРАТУРОПРОВОДНОСТЬ As_2Se_3 В ДИАПАЗОНЕ ТЕМПЕРАТУР ОТ КОМНАТНОЙ ДО ТЕМПЕРАТУРЫ ПЛАВЛЕНИЯ

В работе приведены результаты измерения температурной зависимости теплопроводности и температуропроводности As_2Se_3, как чистого, так и допированного с In и Ag. Измерения проводились нестационарным методом на малых плоскопараллельных образцах (по $1,4 \times \times 5 \times 5$ мм^3 и меньше) в диапазоне температур от комнатной до температуры плавления. Полученные результаты для теплопроводности сильно отличаются от тех, которые можно получить стационарными методами. Они также отличаются от результатов, полученных другими нестационарными методами для различных халькогенидных стекол. Используя измеренные значения теплопроводности и температуропроводности, мы вычислили теплоемкость единицы объема. Она сравнена с удельной тепловой емкостью, измеренной другими авторами при использовании другого независимого метода.