

## LOW-TEMPERATURE THERMAL PROPERTIES OF Ge-As-S GLASSES

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A parallel study of the low-temperature specific heat,  $C_p$  and thermal conductivity,  $k$ , of  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses is carried out. A comparison with our previous results concerning the compositional dependences of other thermal properties is made. A new scaling law for the parameters of the  $C_p/T^3$  peak is established, and a relation between the temperature dependence of the calculated thermal diffusivity with a parameter characterizing the plateau of  $k$  is established. A correlation between the fragility of the studied glasses and the parameters of the low temperature thermal properties is found, based on the influence of the excess quasi-localized vibrational excitations in a defined temperature range.

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### 1. Introduction

The characteristic and universal features of the thermal properties of the glasses above a few Kelvin, and the models advanced for their explanation, are still a matter of interest and debate [1-4]. There are scarce data for the specific heat,  $C_p$ , and the thermal conductivity,  $k$ , of the chalcogenide glasses. A joint study of both these properties has been performed on binary chalcogenide systems [5], and no parallel studies are known for ternary Ge-As-S systems. Recently, we have studied the compositional dependences of various thermal properties of the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses. These are the thermal diffusivity,  $D$ , at 300 K [6], the changes of the specific heat,  $\Delta C_p$  at the glass transition temperature,  $T_g$  [7], the low-temperature specific heat,  $C_p$  [8] and the thermal conductivity,  $k$  [9]. It is well known that the large changes of the specific heat,  $\Delta C_p$  at  $T_g$  imply a more fragile character in the "strong to fragile" characteristics of the glasses. In the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  system, where the mean coordination number,  $Z$  varies from 2.4 to 2.8,  $\Delta C_p$  at  $T_g$  increases abruptly when  $Z$  increases from 2.67 to 2.80 and increases more slowly when  $Z$  decreases from 2.5 to 2.4, i.e. according to Ref. [7] the strongest glasses of this system are between  $Z = 2.5$  and 2.7. The thermal diffusivity measured at 300 K [6], also shows an increase in the  $Z$  ranges towards 2.8 and 2.4. Now we can assume that the lowest  $D$  values are typical of the strongest, less fragile, glasses. Our recent studies of the low-temperature specific heat  $C_p$  of the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses deal with the peak in the  $C_p/T^3$  vs.  $T$  plot. This universal feature is related to a peak in the density of states at low frequencies, connected with an excess of low-temperature vibrations in the glassy state, known as the Boson peak. Its parameters depend on  $Z$  [8]. The low-temperature thermal conductivity,  $k$ , exhibits the universal "plateau", where  $k$  is either constant or changes slightly with  $T$ . The parameters of the plateau depend also on  $Z$  [9]. Here we compare the data for  $C_p$  and  $k$ , and give new results for a correlation between the fragility and many parameters of the low-temperature thermal properties of the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses.

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On the basis of the tunneling model and the soft potential model [3], the reasons for the appearance of this correlation are discussed.

## 2. Experimental details

The data for the  $C_p$  measurements were obtained by a heat pulse method, using an adiabatic vacuum calorimeter. The relative accuracies were about 1% and 5% in the temperature ranges 5-60 K and 3-5 K, respectively [8]. The thermal conductivity measurements were carried out automatically by the stationary heat flux method. The error was below 3% [9].

## 3. Results and discussion

The low-temperature dependences of the specific heat in the  $C_p/T^3$  vs.  $T$  plot and of the thermal conductivity,  $k$  taken from our preliminary results [8, 9] are presented in double logarithmic scale and combined in Figs. 1a and 1b, respectively. The comparison of Fig. 1a with Fig. 1b displays non-monotonic changes of  $C_p/T^3$  and  $k$  with the composition of the studied system. Moreover, the changes of  $k$  are inverse and stronger than those of  $C_p/T^3$ , as is expected [5]. While the peak value  $(C_p/T^3)_{\max}$  decreases 1.6 times from  $x = 30$  to  $x = 38$ , the  $k$  value at  $T_{\min}^k$ , the temperature of the end of the plateau (defined by the straight line in Fig. 1b) increases 2.7 times and 3.1 times at  $T_{app}$ , the temperature of the appearance of the plateau. The used scale allows us to obtain from Fig. 1a the often discussed dependence between  $(C_p/T^3)_{\max}$  and  $T_{\max}$ , the temperature at which maxima appear. We find that in the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  system  $(C_p/T^3)_{\max} \sim T_{\max}^{-3.4}$  (inset in Fig. 1a). This dependence differs from the scaling relation obtained for a wide set of materials, including crystalline ones presented in [10]. There the exponent is -1.6, while in the studied Ge-As-S system it is -3.4, in accordance with the fact that at  $T_{\max}$  we find  $C_p \sim T_{\max}^{-0.4}$ . It also could be concluded that there is not a close relation between the  $C_p/T^3$  maxima in disordered and ordered materials, because of the different natures of the low-energy vibration spectra of glasses and crystalline solids, as supposed in [3]. The comparison of the figures also shows that  $(C_p/T^3)_{\max}$  is not located at the center of the plateau, and the values of  $T_{\max}$  are near to those of  $T_{app}$ , which were specified by us [9] using dependences in the framework of the soft potential model (SPM). Here, we have found the  $x$  and  $Z$  dependences of the thermal conductivity at  $T_{app}$ . A well-expressed increase of  $k_{app}$  is seen when  $Z$  increases from 2.7 to 2.8, and a slighter one occurs when  $Z$  decreases towards 2.4 (inset in Fig. 1b). The established  $Z$  dependence of the parameter  $k_{app}$  of the universal plateau is similar to the  $Z$  dependence of the values of  $k$  before its increase after the end of the plateau,  $k_{\min}$ , and for the respective temperature  $T_{\min}^k$ , both found in [9]. The evaluated Debye temperatures, which mark in Fig. 1b the changes to a nearly linear slope at the high temperature end of the  $k$  vs.  $T$  dependences, also have a similar  $Z$  dependence to that given in [9]. The  $Z$  dependence of the parameter  $T_{\max}$  of the characteristic  $C_p/T^3$  peak [8], as well as the established  $Z$  dependence of  $D$  at various temperatures (Fig. 2a, discussed below) also has a similar nature. Only the  $(C_p/T^3)_{\max}$  dependence on  $Z$  shows an opposite form, with maximal values in the middle  $Z$  range, as expected owing to the fact that  $C_p$  increases when  $k$  decreases. All these results lead to the conclusion that the parameters of the low-temperature thermal properties conclusively correlate with the  $Z$  dependence of the fragility of the glasses from the  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  system [7, 11].

Using our experimental data for  $k$  between 4.2 and 300 K [9], for  $C_p$  within 5-70 K [8] and unpublished data for  $C_p$  within the range 70-300 K, we have calculated the values of the diffusivity  $D$  for the studied compositions at selected temperatures, on the basis of the well known relation  $D = k/\rho C_p$ , where the density  $\rho$  was taken from [12]. The established  $Z$  dependences shown in Fig. 2a follow a similar behaviour to that found by us [6] for the  $Z$  dependence of  $D$  at room temperature, as plotted in the same figure. The calculated temperature dependences of  $D$  for some compositions are presented in Fig. 2b. Two new results can be pointed out: (i) the diffusivity decreases abruptly in the low temperature range, being nearly proportional to  $T^2$ , and (ii) this decrease almost stops at the temperatures marked with arrows. These temperatures are just those at the end of the plateaux,  $T_{\min}^k$ , of the respective compositions. The parallel studies of  $C_p$  and  $k$  have obviously shown an interesting

relationship between  $T_{min}^k$  and the form of the temperature dependence of  $D$ , which will be discussed in a further study.

If there is a correlation between the fragility and the thermal properties, the problem is to identify the reasons for its appearance and extent. The features of the specific heat have been explained taking into account that at the lowest temperatures, according to the tunneling model the

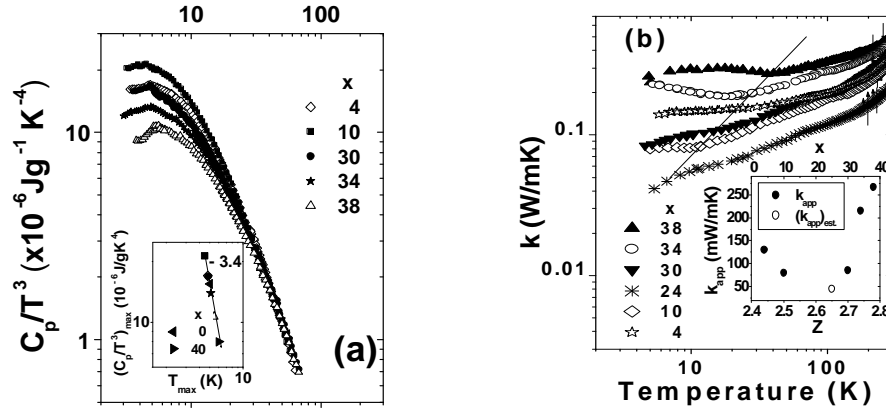


Fig. 1. Temperature dependences, for  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses, of: (a)  $(C_p/T^3)$ ; the inset –  $(C_p/T^3)_{\max}$  vs.  $T_{\max}$  (b) thermal conductivity  $k$ ; the inset –  $k_{\text{app}}$  vs.  $Z$ .

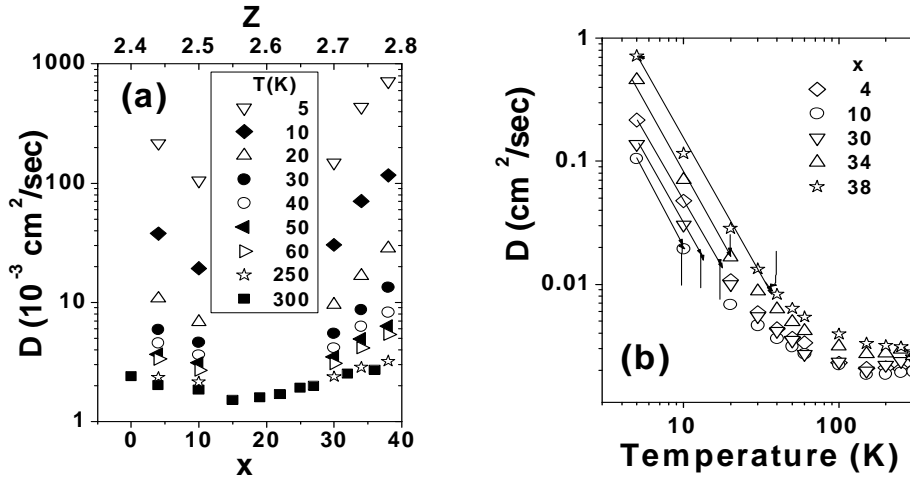


Fig. 2. Compositional (a) and temperature (b) dependences of the thermal diffusivity  $D$ . The arrows in (b) mark the temperature at the end of the plateau in  $k(T)$ ,  $T_{min}^k$ .

two-level states (TLS) give a linear contribution  $C_{\text{TLS}}T$  to  $C_p$ , besides the cubic Debye contribution  $C_D T^3$  due to the extended long-wavelength vibrations [3]. If one accepts that  $C_p = C_1 T + C_3 T^3$ , the coefficient  $C_3$ , related to the Debye contribution, can be obtained from a  $C_p/T$  vs.  $T^2$  plot. However,  $C_3$  should be higher than the real Debye coefficient, because of the failure to take into account the third contribution of the additional quasi-localized vibrations, the soft modes (SM) responsible for the Boson peak. In accordance with the SPM, it has been accepted that  $C_p = C_{\text{TLS}}T + C_D T^3 + C_{\text{SM}} T^5$  [3]. We have found the difference between  $C_3$  and the coefficient  $C_D$  calculated by the classical model, for the studied system [9]. Fig. 3a shows the  $Z$  dependence of the difference  $(C_3 - C_D)$ . It can be concluded that the soft mode contributions are the highest for glasses in the middle  $Z$  range, i.e. for the less fragile glasses. Increased with the SM contributions, the  $C_p$  values have a similar  $Z$  dependence at temperatures around that of the  $C_p/T$  peak. Fig 3b displays the  $Z$  dependence of the normalized  $C_p$  values. It is not so well expressed above 20 K, and nearly disappears above 55 K. This can be connected with the temperature extent of the soft mode contribution. Also, the

normalized  $k$  values show a decrease in their differences with  $Z$  at  $T > 50$  K (Fig. 3c). However, it is substantially lower than that of  $C_p$ . Probably, the  $Z$  dependence of  $k$  is not mainly governed by the SM. This influences, to some degree the  $Z$  dependence of the  $D$  values (Fig. 3d).

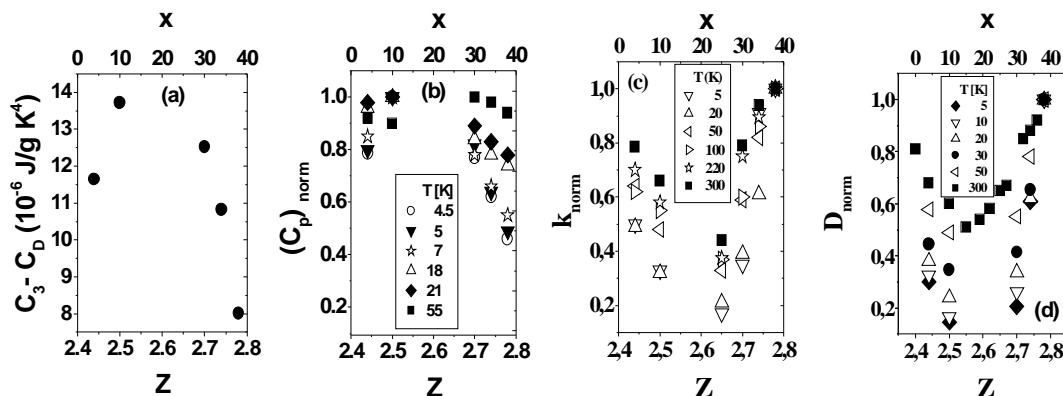


Fig. 3. Concentration and  $Z$  dependences of (a) specific heat coefficient differences ( $C_3 - C_D$ ) and of (b) the specific heat  $(C_p)_{\text{norm}}$ , (c) the thermal conductivity  $k_{\text{norm}}$ , (d) the thermal diffusivity  $D_{\text{norm}}$ , normalized to their maximum values at the selected temperatures.

#### 4. Conclusions

Parallel studies of the low-temperature specific heat and the thermal conductivity in  $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$  glasses have revealed the peculiarities of the compositional and  $Z$  dependences of the parameters of the characteristic  $C_p/T^3$  peak and the universal plateau of  $k$ , as well as of the calculated thermal diffusivity. Conclusive proofs for a correlation between the fragility of these glasses and the parameters of their low-temperature features are given, connected with the excess quasi-localized soft modes in a definite temperature range. A new scaling law between  $(C_p/T^3)_{\text{max}}$  and  $T_{\text{max}}$  as well as special features in the temperature dependence of  $D$  are found.

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