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Thermal diffusivity of Ge-As-Se(S) glasses

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The thermal diffusivity of bulk $Ge_xAs_{40-x}Se(S)_{60}$ glasses has been measured by an optical beam deflection method as a function of the composition. The dependence of the thermal diffusivity of both the families on the average coordination number Z has a complex behavior and is interpreted in the frame of chemical and structural ordering of glasses. [S0163-1829(97)06618-6]

INTRODUCTION

The structure of chalcogenide glasses has been a subject of extensive studies during the last decades. The lack of translational regularity and of methods of identifying nonperiodic atomic configurations in noncrystalline solids stimulates compositional investigations of different physical and structural properties of glasses. The idea of using the average coordination number Z to interpret the compositional dependences of these properties[1,2] allows the importance of the topological structure to be put in evidence. By comparing the degrees of freedom of the atoms with the number of the linear independent constraints, a notion of underconstrained (floppy) and overconstrained (rigid) amorphous solids was introduced. At $Z=2.4$ the two quantities are equal and the structure of glasses percolates. Special features have been found in the property-composition dependences at $Z=2.4$, due to the floppy-to-rigid transition. Besides, data for different physicochemical, optical, and structural properties in binary and ternary glasses exhibit peculiarities at $Z=2.67$, connected with a structural phase transition,[3] due to the medium-range ordering. At $Z=2.67$ the structure goes from a fully developed two-dimensional (2D) layerlike structure to a three-dimensional network. This is supported also by experimental data for $Ge_xAs_{40-x}S(Se)_{60}$ glasses.[4,5]

Thermal diffusivity of chalcogenides has been widely studied in the past years.[6–12] This interest is stimulated by the fact that thermal diffusivity and/or conductivity is very sensitive to the structure of solids. In fact, thermal conductivity in nonmetals is connected to the vibrations of the atoms in the network around their equilibrium position and structure changes are expected to influence the heat diffusion process. In this paper we present results on the thermal diffusivity compositional dependence of glasses from two families: $Ge_xAs_{40-x}S(Se)_{60}$. At $x=0$ and $x=27$ the average coordination number Z is 2.4 and 2.67, respectively. At $Z=2.4$ the expected mechanical threshold coincides with a chemical ordering effect[13,14] and at $Z=2.67$ no chemical ordering exists in our two families, which belong to the pseudobinary line $[As_2S(Se)_3]_x[Ge_2S(Se)_3]_{1-x}$. Thus, the influence of the chemical and topological thresholds has been assessed by comparing the behavior of the systems near $Z=2.4$ and $Z=2.67$.

The bouncing configuration of the optical beam deflection (OBD) method is used to measure the thermal diffusivity of the samples.[15,16] The main advantage of this method to the photoacoustic cell technique,[6–12] widely used to determine the thermal diffusivity of chalcogenide glasses, is that bulk samples as well as thin films can be measured by it.

EXPERIMENTAL DETAILS AND DATA ANALYSIS

The glasses were prepared by a standard melt quenching method. Appropriate amounts of 99.999% pure Ge, As, and Se(S) were sealed in quartz ampoules at 10^{-3} Torr and mixed in a furnace for 30 h. The samples were held at temperature above 800° for at least 12 h. The samples compositions were verified by energy-dispersive x-ray analysis and their amorphous structure was proven by x-ray diffractometer.

The setup used for the present study was a normal mirage setup. The heating laser (Ar^+ or $He\text{-}Ne^+$) beam of about 5 mW was modulated by a mechanical chopper at a frequency between 6 and 15 Hz and was focused at the sample surface to a $1/e$ radius of about 45 μm. The beam of a probe 0.6 mW $He\text{-}Ne^+$ laser fell on the sample surface at a small ($\sim 2^0$) angle measured from the surface. Its $1/e$ waist radius was about 32 μm. When this beam passes through the heated area of air near the sample surface, it is refracted by the time varying index of refraction, so that the direction of the reflected beam oscillates. These oscillations were detected by a quadrant cell and the signal was fed to a lock-in amplifier (PARC 5301). The intensities of both the heating and the reflected probe beams were measured and were used to normalize the experimental results. The sample was mounted on a three-dimensional stage with an accuracy of 1 μm.

In our experiments the samples thickness was more than four times greater than the thermal diffusion length, so that they were considered thermally thick. Data from ellipsometric measurements showed that the optical absorption length ($1/e$ decay) of the heating beam was about 0.1–0.2 μm, which is much less than the thermal diffusion length in the samples (120–180 μm). We assumed that the light was absorbed at the samples surface. Under these conditions the OBD signal is given by[15]

$$\varphi_{t,n}=C\int_{-\infty}^{\infty}\frac{e^{i\lambda s}}{q_s}\,\Phi_{t,n}d\lambda, \tag{1}$$

$$\begin{pmatrix}\Phi_t\\ \Phi_n\end{pmatrix}=\begin{pmatrix}i\lambda\\ -q_g\end{pmatrix}\left[\operatorname{erfw}\left(\frac{q_gR_p}{2}-\frac{h}{R_p}\right)\pm\operatorname{erfw}\left(\frac{q_gR_p}{2}+\frac{h}{R_p}\right)\right]$$

$$\times\exp\left(-\frac{(R_h^2+R_p^2)\lambda^2}{4}\right).$$

Here φ_t and φ_n refer to the transverse and the normal components of the deflection of the probe beam, respectively; R_h and R_p are the radii of the heating and the probe beams, q_s and q_g are the thermal wave numbers in the sample and in the air $[q_{s,g}=(\lambda^2+2\pi if/\alpha_{s,g})^{1/2}$, where $\alpha_{s,g}$ are the thermal diffusivities of the sample and the air, i is the imaginary unit, f is the modulation frequency, and λ is the spatial frequency]. C is a constant and s is the distance between the heating and the probe beams (Fig. 1). The function erfw(z) is defined as

$$\operatorname{erfw}(z)=\frac{\sqrt{\pi}}{2}\exp(z^2)\operatorname{erfc}(z)$$

and erfc(z) is the complementary error function.

After normalizing the experimental data magnitudes, they were fitted to Eq. (1) by a least-squares multiparameter fitting procedure (simplex method) on a DEC-Alpha 500 minicomputer. Two procedures were applied to increase the accuracy and the reliability of the obtained results.[16] First, although the beams radii and h were measured with an accuracy of 1 μm, they were considered unknown and obtained together with the thermal diffusivity of the sample, as a result of the fitting. Besides, data sets obtained at different frequencies and/or heights of the probe beam were fitted simultaneously. Usually, four sets of data were used.

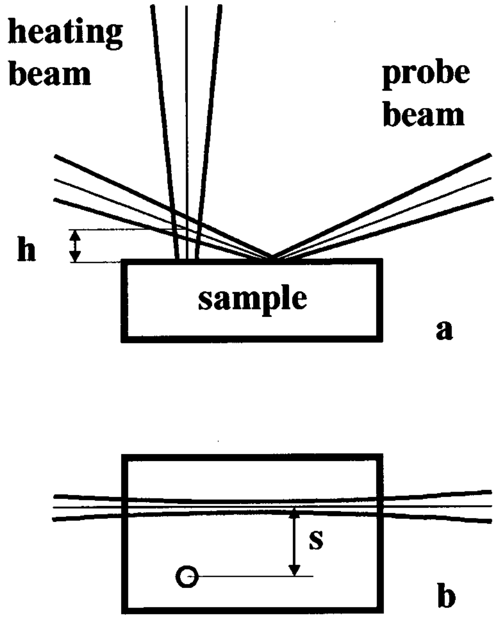

FIG. 1. A schematic picture of the position of the probe and the heating beams of the bouncing OBD configuration: (a) side view, (b) front view.

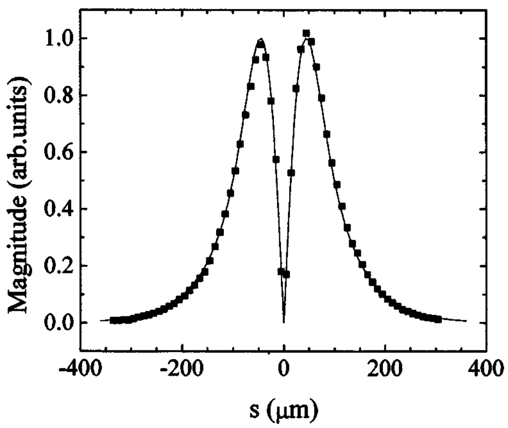

FIG. 2. The measured magnitude of the transverse OBD signal and the fitted theoretical curve for $Ge_{25}As_{15}Se_{60}$.

Figure 2 shows experimental results for a transverse OBD signal for the sample $Ge_{25}As_{15}Se_{60}$ and the respective theoretical curve (1), obtained from the fitting procedure. The variance of the fitting, given by

$$\mathrm{var}=\frac{\Sigma(\varphi_i^e-\varphi_i^t)^2}{\Sigma(\varphi_i^e)^2},$$

is used as a measure of the goodness-of-fit. Here φ_i^e and φ_i^t are the experimental and the theoretical values. The variance was between 0.004 and 0.0006, but most frequently it was about 0.001, as in the example shown in Fig. 2.

The obtained results for the thermal diffusivities of the families $Ge_xAs_{40-x}Se_{60}$ and $Ge_xAs_{40-x}S_{60}$ are shown in Fig. 3 and Table I. The experimental points are those obtained from the fit of all data related to one sample, measured at different frequencies and heights, and the error bars indicate the lower and upper values obtained from a single measurement at a given frequency and h. The difference between these values does not exceed 5% for the Ge-As-Se family,

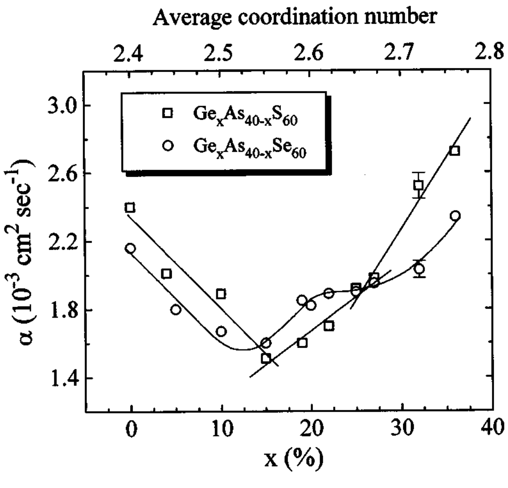

FIG. 3. Thermal diffusivity of $Ge_xAs_{40-x}Se_{60}$ and $Ge_xAs_{40-x}S_{60}$ glasses as a function of composition.

TABLE I. Values of the average coordination number and the thermal diffusivity of $Ge_xAs_{40-x}S_{60}$ and $Ge_xAs_{40-x}Se_{60}$ glasses.

Ge concentration (%)	Z	Thermal diffusivity of $Ge_xAs_{40-x}S_{60}$ (10^{-3} cm^2 s^{-1})	Thermal diffusivity of $Ge_xAs_{40-x}Se_{60}$ (10^{-3} cm^2 s^{-1})
0	2.40	2.40	2.16
4	2.44	2.01	
5	2.45		1.80
10	2.50	1.89	1.67
15	2.55	1.51	1.60
19	2.59	1.60	1.85
20	2.60		1.82
22	2.62	1.70	1.89
25	2.65	1.92	1.90
27	2.67	1.98	1.95
32	2.72	2.52	2.03
36	2.76	2.72	2.34

but for some Ge-As-S samples it was 7%. These values can be compared with the confidence intervals of α, obtained from data fitting. When using all data for a given sample to fit the parameters, the 68% confidence intervals are ±2–4 % from the data given in Fig. 3 and Table I.

DISCUSSION

The thermal diffusivity variation with Z can be interpreted on the bases of change in the chemical ordering and in the network topology. Our results show a complex behavior. At $Z>2.4$ α first decreases but at $Z>2.55$ an increase in α with the increment of the average coordination number can be seen. Besides, a change in the slope in the $\alpha(z)$ dependence of the Ge-As-S family is evident at $Z\approx 2.67$. The three regions are indicated by straight lines, obtained from linear fitting of the corresponding data. In the Ge-As-Se family all the changes in the α values are relatively weaker, and the increment of the slope goes through an inflection point near $Z=2.67$, as can be seen from the line given as a guide to the eye.

Because $As_2Se(S)_3$ are stoichiometric compositions, the α values at $Z=2.4$ can be influenced by the chemical ordering of the compounds. At $Z>2.4$ the incorporation of Ge disorders the dense packing of the molecular structure and a decrease of α should be expected. With increasing Z not only As-based but also Ge-based quasimolecular species are formed. The $AsSe(S)_{3/2}$ pyramidal units and the $GeSe(S)_{4/2}$ tetrahedra begin to connect in a layerlike structure. This may be the reason for the broad minimum near $Z=2.55$ and the thermal diffusivity increase with the further increment of Z.

If Z increases up to 2.67 the layerlike structure is expected to be fully evolved and a cross-linking begins,[3] which can change the $\alpha(Z)$ dependence. We have found extrema or inflexions at $Z\approx 2.67$ in glasses and thin films from the investigated systems in various physicochemical, optical, and structural compositional dependences,[4,5,17,18] which are connected with the topological 2D-3D transition. In the Ge-As-S family the features are better expressed than in the more compact Ge-As-Se family. The investigations of $Ge_xAs_{40-x}S_{60}$ with differential scanning calorimetry showed a well expressed increase of the specific-heat capacity **ΔCp** at the glass transition temperature[19] after $Z=2.67$. It is interesting to point out that **ΔCp** shows a slight decrease at $Z>2.4$, which stops around $Z=2.55$. The influence of the chemical ordering and its disturbance is also expressed in other property-composition dependences. So, in the Z dependence of the integrated intensity of the first sharp diffraction peak of Ge-As-Se thin films (fresh and annealed), a decrease at $Z>2.4$ and a broad minimum around $Z=2.55$ are seen, as well as peculiarities around $Z=2.67$.[20] That is why a plausible explanation of the change of the slope of the $\alpha(Z)$ curves around $Z=2.67$ is the proposed topological phase transition[3] from a two-dimensional to a cross-linked three-dimensional network structure.

The thermal diffusivity of several sets of binary and ternary chalcogenides have been measured.[6–12] At the stoichiometric compositions ($Z=2.4$) α shows a well expressed maximum for all binary glasses, Ge-Te,[6,9] As-Te,[10] Ge-Se.[11] The decrease of α at $Z>2.4$ is attributed to a chemical ordering change and is consistent with our results. In the As-Te-Se system,[7] the highest values of the thermal conductivity have also the stoichiometric samples $(As_2Se_3)_x(As_2Te_3)_{1-x}$, with $Z=2.4$. But for the systems $Ge_xSb_{5(10)}Se_{95(90)-x}$,[8] there are no stoichiometric samples with $Z=2.4$ and no maximum connected with chemical ordering effects can be seen at this point. Maxima appear at $Z\approx 2.67$, where the composition $Ge_{25}Sb_{10}Se_{65}$, which exhibits the highest thermal diffusivity of the family $Ge_xSb_{10}Se_{90-x}$, may be written as $(Sb_2Se_3)_x(GeSe_2)_{1-x}$ with $x=1/6$. The sample $Ge_{27.5}Sb_5Se_{67.5}$, with the highest value of α in the family $Ge_xSb_5Se_{95-x}$, cannot be written in the same form but its composition is closer to the stoichiometric one than any other sample from the family. It is seen that in this case the expected topological phase transition coincides with the chemical ordering in the system. In our case no chemical ordering exists at $Z=2.67$ and the change in the thermal diffusivity dependence on Z can be connected only with topological changes.

The results shown in Fig. 3 can also be compared with the compositional dependence of the elastic properties of chalcogenide glasses. There is a simple relation between the thermal diffusivity of insulators and semiconductors and the velocity of the sound (long-wave phonons):

$$\alpha=\frac{1}{3}\,\overline{V}\overline{n}, \tag{2}$$

where $\overline{V}$ and $\overline{n}$ are the average sound velocity and the average free path of the phonons.[21] It seems that in amorphous solids at temperatures above 100 K, the low limit of $\overline{n}$ is the interatomic spacing.[22] When applying Eq. (2) to our samples using $\overline{V}\approx 2000$ m/s, which is a typical value for the sound velocity in chalcogenides, one obtains $\overline{n}\approx 3$ Å. This is near the bond lengths in chalcogenide glasses.[3] $\overline{V}$ is given by

$$\overline{V}=\sqrt{\frac{1}{\rho}\,\frac{\varepsilon K(1-\mu)}{(1+\mu)}}. \tag{3}$$

Here K is the bulk modulus, ρ is the density, and μ is the Poisson's ratio. The coefficient ε is introduced to account for the fact that $\bar{V}$ is a combination of longitudinal and transverse sound velocities. $\bar{n}$ may be expressed approximately as $\bar{n}=\sqrt[3]{\nu_a}$, where ν_a is the atomic volume. The values of ρ have been measured and ν_a were calculated for the investigated samples.[5] Both of them vary by 5–6 %. Taking into account that μ is also a weak function of the sample microstructure, one can approximately write $\alpha \propto \sqrt{K}$.

Many investigations of Ge-As-Se(S) glasses show an increment of the bulk or longitudinal moduli with Z. After $Z=2.67$ the curves change the slope and the increment become more rapid.[23–27] At the same time the system As-Se has been shown to have a maximum of the bulk modulus at the stoichiometric composition As_2Se_3.[3]

CONCLUSION

We have investigated thermal diffusivities of $Ge_xAs_{40-x}Se(S)_{60}$ glasses by an OBD method. The Z dependence of the diffusivities shows a broad minimum near $Z=2.55$, which may be explained by the disturbance of the chemical ordering around $Z=2.4$. Peculiarities exist also around $Z\approx 2.67$, which are attributed to a structural phase transition from a 2D to a 3D network structure, better expressed in the $Ge_xAs_{40-x}S_{60}$ family.

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[1] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).
[2] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).
[3] K. Tanaka, Phys. Rev. B **39**, 1270 (1989).
[4] D. Arsova, E. Skordeva, and E. Vateva, Solid State Commun. **90**, 299 (1994).
[5] E. Vateva, D. Arsova, E. Skordeva, and E. Savova, in *Electronic, Optoelectronic and Magnetic Thin Films*, edited by J. Marshall, N. Kirov, and A. Vavrek (Wiley, New York, 1995), p. 604.
[6] J. C. M. Lima, N. Cella, L. C. M. Miranda, C. Chying An, A. H. Franzan, and N. F. Leite, Phys. Rev. B **46**, 14 186 (1992).
[7] K. Nandakumar and J. Philip, J. Non-Cryst. Solids **144**, 247 (1992).
[8] A. Srinivasan, K. N. Mandhusoodanan, E. S. R. Gopal, and J. Philip, Phys. Rev. B **45**, 8112 (1992).
[9] K. Madhusoodanan, J. Philip, G. Parthasarathy, A. Asokan, and E. S. R. Gopal, Philos. Mag. B **58**, 123 (1988).
[10] K. Madhusoodanan, J. Philip, S. Asokan, and E. S. R. Gopal, J. Mater. Sci. Lett. **7**, 1333 (1988).
[11] K. Madhusoodanan and J. Philip, Phys. Status Solidi A **108**, 775 (1988).
[12] A. K. Ghosh and B. K. Chaudhuri, J. Appl. Phys. **79**, 723 (1996).
[13] S. Mahadevan and A. Giridhar, J. Non-Cryst. Solids **110**, 118 (1989); **143**, 52 (1992).
[14] A. Giridhar and S. Mahadevan, J. Non-Cryst. Solids **134**, 94 (1991).
[15] J. Rantala, Lanhua Wei, P. K. Kuo, J. Jaarinen, M. Luukkala, and R. L. Thomas, J. Appl. Phys. **73**, 2714 (1993).
[16] T. R. Anthony, W. F. Banholzer, J. F. Fleisher, Lanhua Wei, P. K. Kuo, R. L. Thomas, and R. W. Pryor, Phys. Rev. B **42**, 1104 (1990).
[17] E. Vateva, E. Skordeva, and D. Arsova, Philos. Mag. B **67**, 225 (1993).
[18] D. Arsova, E. Vateva, E. Skordeva, and V. Petkov, Solid State Commun. **98**, 595 (1996).
[19] E. Vateva (unpublished).
[20] E. Vateva, D. Arsova, and E. Skordeva (unpublished).
[21] J. R. Drabble and H. J. Goldsmith, *Thermal Conduction in Semiconductors*, 1st ed. (Pergamon, Oxford, 1961).
[22] J. W. Vandersande and G. Wood, Contemp. Phys. **27**, 117 (1986).
[23] K. Tanaka, Solid State Commun. **60**, 295 (1986).
[24] B. L. Halfpap and S. M. Lindsay, Phys. Rev. Lett. **57**, 847 (1986).
[25] R. Boolchand, Phys. Rev. Lett. **57**, 3233 (1986).
[26] R. Ota, G. Yamate, N. Soga, and M. Kunugi, J. Non-Cryst. Solids **29**, 67 (1978).
[27] D. T. Tsiulgyanu, A. D. Dragich, and N. A. Gumeniuk, J. Non-Cryst. Solids **155**, 180 (1993).