

Low Frequency Processes of Dielectric Relaxation in $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ Glassy System

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Abstract: Low-frequency processes of dielectric relaxation were studied in $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ glassy system. The existence of distribution of relaxators over relaxation times is found in line with the Cole-Cole Model for the case of symmetric distribution of relaxation times. The activation energy of dielectric relaxation was equal to $E_p = 0.40 \pm 0.01$ eV. The observed patterns are explained in terms of the model, according to which the structure of chalcogenide glasses represents a set of dipoles formed by charged defects of D^+ and D^- types.

Key words: Dielectric relaxation, $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ glassy system, low frequency processes, thin films, symmetric, activation energy

INTRODUCTION

Chalcogenide Glassy Semiconductors (CGS) of complex composition attract attention of researchers due to their wide application in micro and optoelectronic devices (Kolobov *et al.*, 2004; Kukretil *et al.*, 2015; Bekheet and Hegab, 2008). The processes of charge transfer and accumulation in CGS of various systems can be associated with the exchange of electrons between the charged defects which can be represented by defects of types D^+ and D^- being the centers with negative correlation energy (Anderson, 1975). The existence of defect states with activation energy of 0.43 eV and concentration of $\sim 10^{16} \text{ cm}^{-3}$ was found in $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ system by thermoactivation spectroscopy methods in the temperature range $T = 260, \dots, 280$ K (Bordovsky and Castro, 2006). The objective of this study was to identify specific features of low-frequency relaxation processes in thin layers of $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ glassy system by the Dielectric Spectroscopy (DS) method. The DS method provides us a tool to discover specific features of polarization processes and their relationships with structural features of the studied material (Avanesyan *et al.*, 2000; Castro *et al.*, 2006, 2009). When two or more references are cited in the same parenthesis, the researchers should be in chronological order. And if they have the same year, they should be in alphabetical order. Moreover, if there is more than one reference of the same researcher and the same year, they should be indicated with letters.

MATERIALS AND METHODS

The elemental composition of samples was studied with Carl Zeiss EVO 40 scanning electron microscope (SEM). The maximum resolution of the microscope is 3 nm. To identify the atomic composition of $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ films, the atomic content spectra were identified in the selected regions of the test samples (Fig. 1). Data on the weight and atomic percentages of chemical elements in the samples are shown in Table 1. Dielectric spectra were evaluated on the films of $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ glasses prepared by vacuum thermal evaporation.

The samples had a sandwich configuration with aluminum electrodes and a contact area of 14.0 mm^2 . The thickness of $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ layers was measured with the ELF Spectro ellipso meter and made $\sim 2.0 \text{ }\mu\text{m}$. Dielectric spectra of the studied layers were measured with the "Concept-81" spectrometer (Novocontrol Technologies GmbH) designed for studying the dielectric and electrical properties of an extensive class of materials. Measurements were taken in the frequency range $f = 10^2, \dots, 10^5$ Hz and the temperature range $T = 273, \dots, 313$ K. The voltage $U = 10^{-1}$ V was applied to the samples.

Spectra of the complex dielectric permittivity were calculated from the impedance spectra, according to the following Eq. 1:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega) C_0} \quad (1)$$

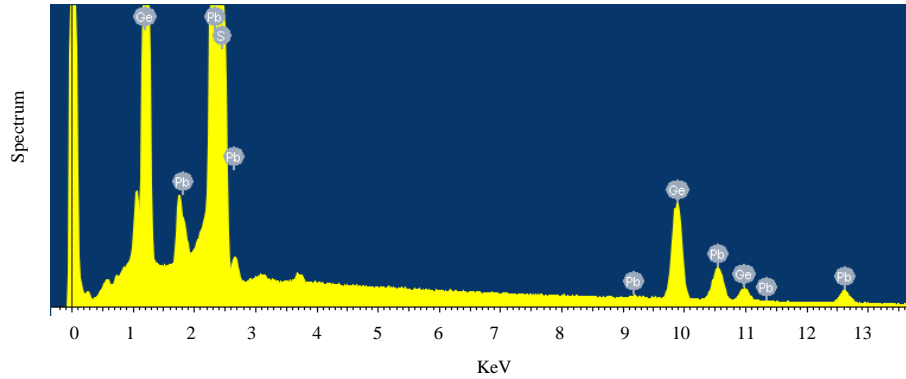


Fig. 1: Spectrum of the atomic content of thin layers in Ge_{28.5}Pb₁₅S_{56.5} system

Table 1: Elemental composition of Ge_{28.5}Pb₁₅S_{56.5} samples (weight % and atomic % content of chemical elements)

Element	Nominal concentration	Mass fraction	Weight (%)	Weight sigma (%)	Atomic fraction(%)
S K	24.80	0.9435	27.29	0.16	56.48
Ge K	32.68	0.9958	34.07	0.24	31.15
Pb M	31.38	0.8428	38.65	0.27	12.38
Total			100.00		

where, $C_0 = \epsilon_0 S/d$ is the capacity of the empty cell. To determine the values of the system relaxation parameters, derived dielectric spectra were approximated by the Havriliak-Negami (HN) two-parametric empirical function (Kremer and Schonhals, 2003) using the NovocontrolWinfit Software. Based on these approximations, positions of the dielectric loss maxima were identified and the HN parameters were determined for the studied relaxation processes:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1+(i\omega\tau)^{\alpha_{HN}}]^{\beta_{HN}}} \quad (2)$$

Where:

ϵ_∞ = The high-frequency limit of the real part of the dielectric permittivity

$\Delta\epsilon$ = The dielectric increment (the difference between the low-frequency and high-frequency ϵ limits)

$\omega = 2\pi f$, α_{HN} and β_{HN} are shape parameters that describe the symmetric ($\beta = 1$, the Cole-Cole distribution) and asymmetric ($\alpha = 1$, the Cole-Davidson distribution) expansion of the relaxation function, respectively.

RESULTS AND DISCUSSION

Measurements of the dielectric loss tangent $\tan\delta$ in Ge_{28.5}Pb₁₅S_{56.5} system layers in the frequency range $10^1, \dots, 10^5$ Hz at different temperatures (Fig. 2) revealed the existence of the loss maximum which shifts to higher frequency areas with increasing temperature. The presence of maxima on the $\tan\delta$ curve at a relatively low

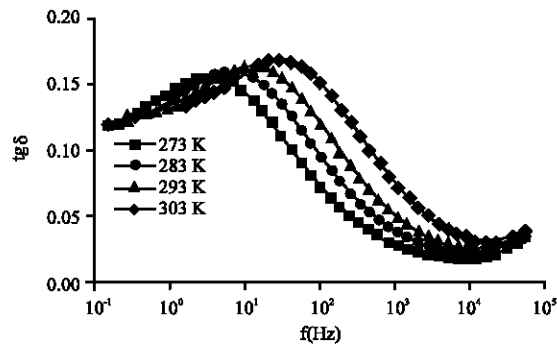


Fig. 2: Frequency dependence of the dielectric loss ($\tan\delta$) at different temperatures

frequency and temperature indicates the existence of the relaxation process responsible for relaxation losses in the samples. The presence of the relaxation process is also evidenced by the maximum on the temperature-dependent dielectric loss curves in the low-frequency regions.

In many dielectrics, relaxation processes are associated with the existence of a set of relaxation times, rather than a single relaxation time. These cases can be viewed as the presence of distributed relaxation times and consequently of activation energies. Such distribution can be associated with the manifestation of relaxation processes of various nature or with the distribution over dipole concentration within the structure. In the case of ionic hopping processes, it is assumed that the potential energy changes after each hop and certain time is needed to return to the minimum potential energy. When the contribution of multiple mobile defects is considered, we obtain a set of relaxation times.

In order to prove the existence of the “non-Debye” dispersion mechanism in the studied system, the Cole-Cole diagram ($\epsilon'' = f(\epsilon')$) was constructed. In our case, the existence of distribution of relaxators over time is manifested in the deviation from the hemispherical dependence with the radius of the hemisphere $(\epsilon_s - \epsilon_\infty)/2$ (Fig. 3).

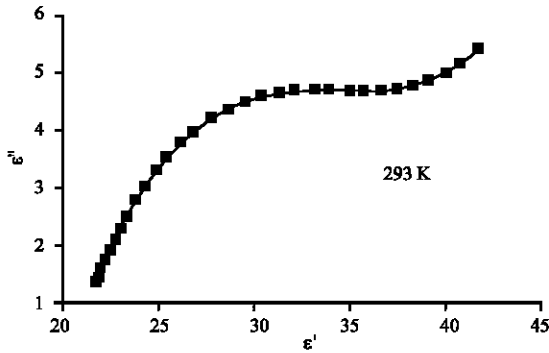


Fig. 3: The Cole-Cole diagram for $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ samples at room temperature

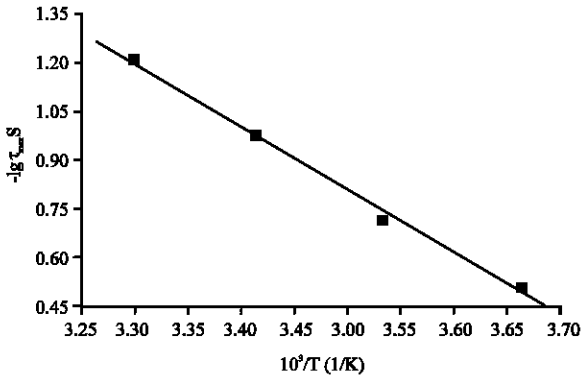


Fig. 4: Temperature dependence for the most probable relaxation time in $\text{Ge}_{28.5}\text{Pb}_{15}\text{S}_{56.5}$ layers

The shape of the dielectric loss curve of the loss factor $\epsilon'' = (f)$ or the dielectric loss tangent $\tan\delta = (f)$ can be used for estimating the distribution of relaxation times. The values of relaxation parameters derived from HN approximations of the experimental curves (2) also confirm the existence of distribution of relaxators in line with the Cole-Cole model for the case of symmetric distribution of relaxation times. The temperature dependence of the frequency (relaxation time) with the maximum observed losses $f_m(\tau_m)$ allows us to determine the experimental activation energy E_a , i.e., the energy barrier to dipole orientation. The activation energy calculated from the temperature dependence for the most probable relaxation time (Fig. 4) was equal to $E_p = (0.40 \pm 0.01)$ eV.

The observed patterns in the temperature and frequency dependences of dielectric losses in the low-frequency region can be explained by the original model suggested by the researchers (Giuntini *et al.*, 1981). According to this model, the structure of chalcogenide glasses represents a set of dipoles formed by the charged defects of D^+ and D^- types. Each dipole has its specific relaxation time which depends on the activation energy required for charge carriers to overcome the potential

barrier. The existence of a potential barrier is determined by the Coulomb interaction between the neighboring defect states that form a dipole. The findings of our study correlate with the conclusions of the researchers (Bordovsky and Castro, 2003) and support the hypothesis of the existence of a defect states spectrum when the electron exchange between the states creates quasi-dipoles responsible for the dielectric permittivity dispersion and dielectric losses in the low-frequency region. The electron exchange can occur, for example, between germanium atoms that are present in both bivalent and tetravalent states in the glass structure (Bordovskii and Castro, 2006).

CONCLUSION

As can be seen from the above, our study has revealed the existence of the dielectric loss maximum which indicates the existence of the relaxation process. The values received for relaxation parameters confirm the existence of distribution of relaxators in line with the Cole-Cole model for the case of symmetric distribution of relaxation times. The activation energy of dielectric relaxation process was equal to $E_p = (0.40 \pm 0.01)$ eV. The observed patterns are explained by the model, according to which the structure of chalcogenide glasses represents a set of dipoles formed by the charged defects of D^+ and D^- types.

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