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Si (Ge)–Se–Te glasses: electrical and acoustic properties

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Ternary $Si_{15}Ge\ (Ga)_5Te_{80}$, $Si_{19.7}Te_{78.7}Se_{1.6}$, $Si_{19.2}Te_{76.8}Se_4$, and $Ge_{19}Te_{72}Se_9$ telluride glasses were synthesized. Electrical, acoustic, acoustooptical properties, and the dispersion of optical transmittance of these films were studied in a wide range of temperatures and frequencies. Comparative analysis of the results obtained is performed. Possible mechanisms of the observed phenomena are discussed. It is shown that $Ge_{19}Te_{72}Se_9$ alloy is quite competitive with $Si_{20}Te_{80}$ alloy for the fabrication of highly efficient acoustooptical devices with a wide range of applications in the medium IR spectral region (2–12 µm).

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1. Introduction

The discovery [1] of high values of the acoustooptical figure of merit M_2 in the binary Si–Te system stimulated the studies of ternary systems of glasses by using the replacement of silicon by germanium (or by gallium) or the anionic replacement of tellurium by selenium. The glasses with the composition $Si_{15}Ge\ (Ga)_5Te_{80}$ with high glass-formation ability were synthesized. They were obtained by air quenching in conical cells $\geq$ 15 mm in diameter. It was found that partial replacement of tellurium by selenium reduces the glass-formation ability in melts of the Si–Se–Te system; therefore, only glasses of the compositions $Si_{19.7}Te_{78.7}Se_{1.6}$ and $Si_{19.2}Te_{76.8}Se_4$ were obtained. The alloy $Si_{18.7}Te_{74.6}Se_{6.7}$ was crystalline and unstable in air because of high hydration. Taking into consideration the structural similarity of Si–Te and Ge–Te glasses, one may expect that the glasses of the latter system should also exhibit high acoustooptical characteristics. However, high glass-formation ability is restricted by the possibility of obtaining a vitreous state for the composition $Ge_{18}Te_{82}$ by cold-water quenching in substituted conical cells 5–6 mm in diameter. If tellurium is partially by selenium (specifically, for the composition $Ge_{19}Te_{72}Se_9$ corresponding [2] to ternary eutectic), one should expect an appreciable increase in the glass-formation ability with retention of a glass structure close to that observed in $Si_{20}Te_{80}$. Experiments confirmed the high glass-formation ability of this composition synthesized in conical cells with $\geq$ 15 mm diameter. Glassy alloys and amorphous films of $Ge_{20}Se_{60}Te_{20}$ composition have been prepared [3] and investigated. They are photo-conductive and obey to Meyer-Neldel rule. A complex study of density ρ_0, refractive index n, temperature dependence of conductivity, and the dispersion of optical transmittance of various alloys ($Si_{15}Ge(Ga)_5Te_{80}$, $Si_{19.7}Te_{78.7}Se_{1.6}$, $Si_{19.2}Te_{76.8}Se_4$, and $Ge_{19}Te_{72}Se_9$) has been performed and a first report was given in [4].

2. Experimental

Technological aspects of the preparation of alloys are described in [1].

Specimens for acoustic, optical, and acoustooptic measurements (4×4×6 mm in size) were prepared by cutting followed by lapping and optical-grade polishing. The specimens were cooled during cutting.

Acoustic absorption was measured by two methods. High-frequency measurements (acoustic frequency f = 90-700 MHz) were performed by the acoustooptic method (λ=3.39 µm); and low – frequency measurement (f =14-150 MHz), by the pulse-echo method.

Acoustic waves were excited by resonant piezoelectric transducers made from lithium niobate or piezoceramics, which were cemented to the corresponding face of the specimen with Nonaq Stopcock glue. We used the fundamental frequency (f = 30 MHz for lithium niobate and 14 MHz for piezoceramics) as well as higher harmonics of the transducer.

In acoustooptic measurements, we used the Bragg diffraction of light from acoustic waves. The acoustooptic figure of merit, M_2, was determined by the Dixon method. With this method, not only the intensity of diffracted light I_I, but also the intensity of transmitted light, I_o, is measured, which excludes of the effect of optical absorption on the results. He-Ne and CO_2 gas lasers (λ =3.39 µm and 10.6 µm, respectively), as well as semiconductor laser (λ =1.87 µm and 3.3 µm) were used as radiation sources.

Optical –absorption coefficient α at various wave - length were calculated from optical - transmission data obtained with Fourier Infrared Spectrophotometer FTIR-8400S.

The data on the velocity of sound were obtained by the microwave - pulse- echo-overlap method.

3. Results and discussion

3.1. Electrical Properties

Temperature dependences of resistivity ρ (T) of $Si_{15}Ge(Ga)_5Te_{80}$, $Si_{19.7}Te_{78.7}Se_{1.6}$, $Si_{19.2}Te_{76.8}Se_4$, and $Ge_{19}Te_{72}Se_9$ are shown in Figs. 1–3. It can be seen that the partial replacement of tellurium by selenium in $Si_{19.7}Te_{78.7}Se_{1.6}$ and $Si_{19.2}Te_{76.8}Se_4$ results (Fig. 1), in contrast to $Si_{20}Te_{80}$ glasses,

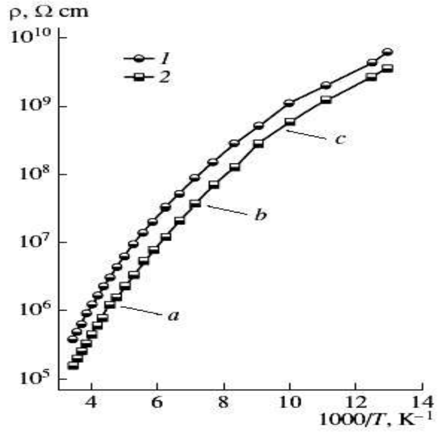

Fig. 1. Temperature dependence of resistivity of glasses: (1) $Si_{19.7}Te_{78.7}Se_{1.6}$ and (2) $Si_{19.2}Te_{76.8}Se_4$. Activation energy E = (a) 0.15, (b) 0.10, (c) 0.06 eV.

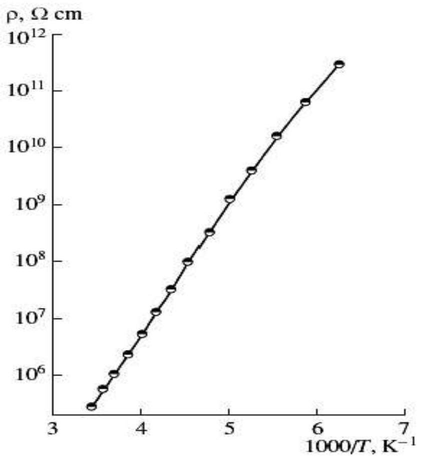

Fig. 2. The temperature dependence of resistivity of $Ge_{19}Te_{72}Se_9$ glass. Activation energy E = 0.44 eV.

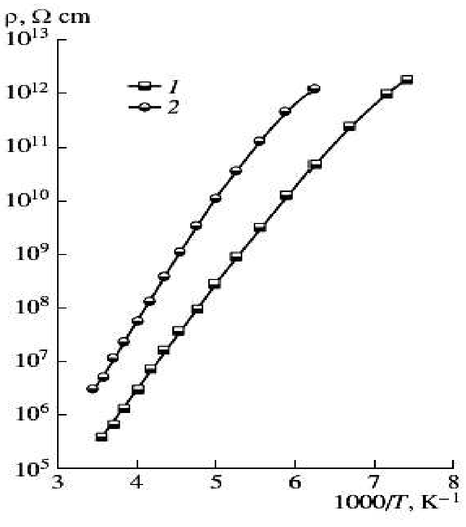

Fig. 3. Temperature dependence of resistivity of glasses: (1) $Si_{15}Ga_5Te_{80}$, E = 0.37 eV; (2) $Si_{15}Ge_5Te_{80}$, E = 0.42 eV.

in the appearance of three ranges where the activation energy E decreases with decreasing temperature, which may be indicative of the increasing role of structural imperfections in alloys. The partial replacement of tellurium with selenium in germanium-containing glass $Ge_{19}Te_{72}Se_9$ essentially increases its glass-formation ability: in this case, the ρ (T) dependence in the entire temperature range is characterized by a single activation energy, which is significantly higher than the values for $Si_{19.7}Te_{78.7}Se_{1.6}$ and $Si_{19.2}Te_{76.8}Se_4$ glasses (Fig. 2). The partial replacement of silicon by germanium or gallium in Si_{15}Ge (Ga) $_5Te_{80}$ glasses does not profoundly affect the glass-formation ability in these glasses, which is consistent with the existence of a single linear part in the ρ (T) dependence (Fig. 3). However, the optical transmittance of these glasses is appreciably (by an order of magnitude) lower than that of $Si_{20}Te_{80}$; therefore, primary emphasis in studying optical photoelastic properties is placed on the $Ge_{19}Te_{72}Se_9$ alloy and, to a lesser degree, on the $Si_{19.7}Te_{78.7}Se_{1.6}$ and $Si_{19.2}Te_{76.8}Se_4$ alloys.

3.2 Acoustic Properties

We measured the velocities of longitudinal sound υ in the glasses synthesized (see Table 1). From the data listed in Table 1, it is seen that the basic matrix of tellurium is predominant in determining the elastic properties of telluride glasses.

The dependence of the sound absorption coefficient α_{ac} on frequency f (Fig. 4) and the dependence of the velocity of sound on temperature (Fig. 5) were obtained only for the $Ge_{19}Te_{72}Se_9$ alloy, because, as will be shown below, this alloy is of greatest interest from the scientific standpoint, and it is also a promising material for the fabrication of acoustooptical devices. In contrast to the $Ge_{19}Te_{72}Se_9$ alloy, $Si_{15}Ge_5Te_{80}$ and $Si_{15}Ga_5Te_{80}$ alloys are found to be fragile (stressed), which is most likely the consequence of high mechanical imperfection.

Comparison of the magnitude and the frequency variations of the sound absorption coefficient of the $Ge_{19}Te_{72}Se_9$ alloy with the previously studied $Si_{20}Te_{80}$ alloy allows two main conclusions to be made. In $Ge_{19}Te_{72}Se_9$ the sound absorption at low frequencies is less and the frequency dependence is steeper, approaching a quadratic low typical of crystals.

Previously, we showed [5] that the large value of the sound absorption coefficient observed in $Si_{20}Te_{80}$, which differs by two orders of magnitude from the values in crystals, and its linear

Table 1. Main elastic parameters of alloys under investigation at T = 300 K.

Composition	v, 10^5 cm/s	ρ_0, g/cm^3	C_{11}, 10^{12} dyn/cm^2
$Ge_{19}Se_9Te_{72}$	2.06	5.41	0.230
$S_{i19.7}Te_{78.7}Se_{1.6}$	2.05	5.1	0.214
$Si_{19.2}Te_{76.8}Se_4$	2.05	5.0	0.210
$Si_{15}Ge_5Te_{80}$	2.04	5.25	0.218
$Si_{15}Ge_5Te_{80}$	2.10	5.29	0.233
$Si_{20}Te_{80}$	2.03	5.03	0.207

frequency dependence (Fig. 4) are the consequences of a specific structure of glasses having a system with two-well structural defects with a broad, almost uniform, distribution of relaxation times. Therefore, the observed value of the absorption coefficient and the character of its frequency variation in the $Ge_{19}Se_9Te_{72}$ alloy under investigation can be attributed to the higher structural quality of this alloy.

With the aim of studying the effect of composition on elastic properties of glasses, we measured the velocity of sound in them and showed that the magnitudes of the modulus of elasticity C_{11} (see Table 1) in $Ge_{19}Te_{72}Se_9$ are larger than in $Si_{20}Te_{80}$. Temperature dependences of the relative change of velocity of sound in these alloys (Fig. 5) also differ. The calculation of the contribution of anharmonicity due to the interaction of a sound wave with thermal phonons by the formula [3] showed (Fig. 5, curve *1*) that it is this interaction which is responsible for the observed temperature dependences of the velocity of sound in $Si_{20}Te_{80}$, provided that the value of the averaged Gruneisen constant (anharmonicity of bonding forces) is $\bar{\gamma}$ = 1.45. The quantities *T* and *Cp* in formula (1) are the temperature and heat capacity at constant pressure, respectively; T_0 = 300 K. The calculation by formula (1) for $Ge_{19}Te_{72}Se_9$ at $\bar{\gamma}$ ~ 1.39 (Fig. 5, curve *2*) shows that attainment of agreement with the experimental data on

$$\frac{(\Delta\upsilon)^{\text{анг}}}{\upsilon(T_0)} = \frac{\bar{\gamma}^2 T_0 C_p(T_0)}{3\upsilon^2(T_0)}\left\{1 - \frac{TC_p\ (T)}{T_0 C_p\ (T_0)}\right\} \quad (1)$$

$\upsilon(T)$ requires the temperature behavior of heat capacity in this alloy to be different from that in $Si_{20}Te_{80}$. Specifically, the slope of this dependence should be steeper at lower temperatures; i.e., $C_p^1(T)/C_p^1(T_0) \approx (T/T_0)^n C_p(T)/C_p(T_0)$, where n = 0.9. This means that the temperature behavior of heat capacity qualitatively approaches the temperature dependences of heat capacity in crystals. This is consistent with the features of frequency variations of absorption in this alloy. As was shown above, the frequency variations of absorption in $Ge_{19}Te_{72}Se_9$ differ from the linear dependences typical of glasses observed in $Si_{20}Te_{80}$ and quantitatively approach the quadratic dependences typical of the crystals in the low-frequency region [3]. This is surprising if one takes into consideration that the increase in the number of components in alloy (as happens in the $Ge_{19}Te_{72}Se_9$ alloy in contrast to $Si_{20}Te_{80}$) is more often than not the prerequisite for the formation of defects, including two-well defects, which are responsible for the specific behavior of the thermal and elastic properties of glasses. However, it is evident that the abovementioned increase in the glass-formation ability induced by the combination of selenium and titanium in tellurium alloy is not the only attractive consequence of this structural ensemble. Most likely, a reduction in the number of defects occurs in such a structure.

3.3 Optical Properties

The low optical transmittance T_0, which only slightly greater than several percent in the transparent region at a wavelength of ~2–20 μm, observed in $S_{i15}Ge\ (Ga)_5Te_{80}$ glasses, in our opinion, the consequence of the inhomogeneity of mechanical properties.

The transmittance of Si–Te allays doped with Se is shown in Fig. 6 (curves *1*, *2*). It is seen that the optical transmittance of these appreciably decreases with increasing Se content. Such transmittance behavior can be explained by the scattering of light by defects, which affect the temperature dependence of resistivity ρ (*T*) (Fig. 1).

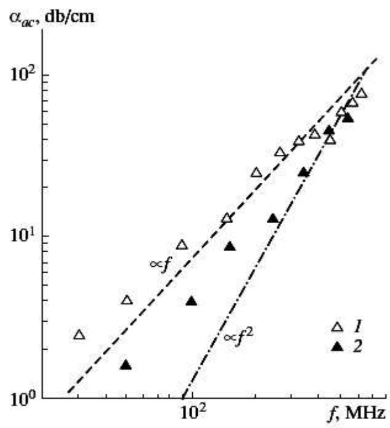

Fig. 4. Coefficient of sound absorption as a function of frequency in glasses: (1) $Si_{20}Te80$, (2)$Ge_{19}Te_{72}Se_9$.

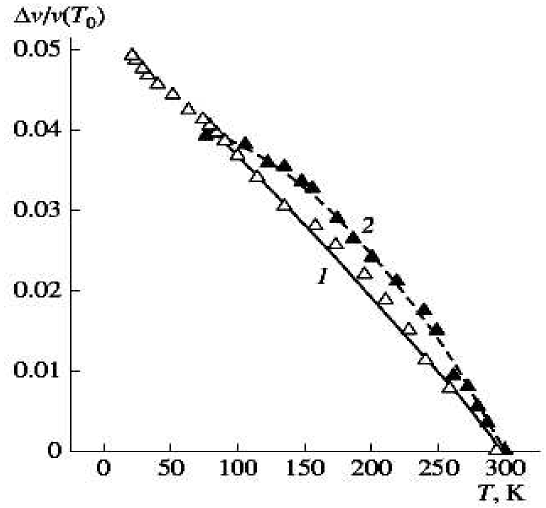

Fig. 5. Temperature dependence of relative change of the sound velocity in glasses: experiment (triangles), theory (lines). (1) $Si_{20}Te_{80}$, (2) $Ge_{19}Te_{72}Se_9$.

The study of the optical properties of the $Ge_{19}Te_{72}Se_9$ alloy showed that minimization of the amount of structural defects observed through acoustic measurements (see above) also manifests itself in this case. First, this alloy exhibits much higher optical homogeneity. Second, within the entire spectral range, the transmittance of this alloy (Fig. 6, curve *4*) is higher than in $Si_{20}Te_{80}$ (Fig. 6, curve *3*). This is most clearly pronounced (Fig. 7) at the wavelengths corresponding to the radiation of a CO_2 laser (10.6 μm), i.e., in the atmospheric transparency window (which is of prime importance).

The value of the refractive index $n = 3.4 \pm 0.02$ for the alloy under study is obtained from the reflection m coefficient. The value obtained is higher than that in the $Si_{20}Te_{80}$ alloy ($n = 3.3$).

3.4 Acoustooptical Properties

It is known that the efficiency of Bragg diffraction of light by ultrasound waves is determined by the acoustooptical figure of merit M_2. In linear mode (low sound intensity), the interaction of light with sound is described as

$$I_1 = (1/2) I_0 M_2 P [\pi d / (\lambda \cos\theta)]^2 \quad (2)$$

$$(M_2)_{tk} = n_t^6 p_{tk}^2 / (\rho_0 v_k^3) \quad (3)$$

where I_1 and I_0 are the intensities of diffracted and incident light, respectively; P is the sound intensity; λ - is the wavelength of light; d is the width of the acoustic beam; θ - is the angle of incidence; n_i is the refractive index; p_{ik} is the component of the photoelastic tensor; ρ_0 is the density of a crystal; v_k is the velocity of a sound wave; i, k = 1, 2, 3, 4, 5, 6; i - is the index of light polarization; and k is the index of deformation in matrix representation.

We showed previously that the $Si_{20}Te_{80}$ alloy has the highest acoustooptical efficiency of Bragg diffraction in a wide range in the near and medium IR region of the spectrum (Table 2). However, the existence of a noticeable optical inhomogeneity in this material called for a further search for ways to optimize its optical properties.

An appreciable improvement of the acoustic parameters (lower sound absorption at the operating acoustooptical frequencies in the region of about 100 MHz; see Table 2) and optical characteristics (lower light absorption, a large refractive index n, and optical homogeneity; see Table 2) observed in the $Ge_{19}Te_{72}Se_9$ alloy makes this alloy very attractive for studying acoustooptical properties.

Preliminary data (Table 2) on the acoustooptical figure of merit M_2 obtained for λ = 3.39 μm show that acoustooptical efficiency in this spectral region is no worse than in $Si_{20}Te_{80}$. From this fact it follows that the new $Ge_{19}Te_{72}Se_9$ alloy is quite promising for the fabrication of new acoustooptical devices. Therefore, more detailed acoustooptical studies in a wider optical spectral range are needed.

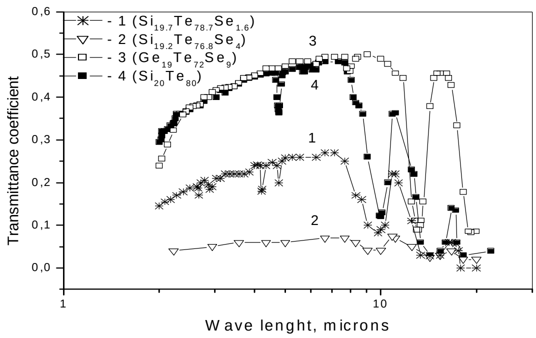

Fig. 6. Dispersion of the optical transmittance coefficient of glasses: (1) $Si_{19.7}Te_{78.7}Se_{1.6}$,(2) $Si_{19.2}Te_{76.8}Se_4$, (3) $Si_{20}Te_{80}$, and (4) $Ge_{19}Te_{72}Se_9$. The thickness of glasses is 6 mm.

Table 2. Acoustooptical parameters of the system of Si (Ge)–Se–Te alloys and other IR materials at T = 300 K.

Material	Transparency range Δλ, μm	α, cm–1	α_{ac}, dB/cm (f = 100 MHz)	λ, μm	Polarization of light with respect to the direction of sound propagation	$(M_2)'$
$Si_{20}Te_{80}$	1.7–13	0.1	8	10.6	‖	3500
				3.39	‖	3200
				1.87	‖	2800
$Ge_{19}Se_9Te_{72}$	2 - 18		4	3.39	‖	3150
Ge	2–20	0.06	0.3	10.6	‖	540
As_2Se_3	0.9–11	1.15		1.15	‖	700
a-Se	1–20	1.15		1.15 10.6	⊥ ⊥	776 692

Note: $(M_2)' = M_2/(M_2)''$, where $(M_2)'' = 1.56 \times 10^{-18}$ s^3/g (M_2 is given for quartz glass); α - is the coefficient of optical absorption.

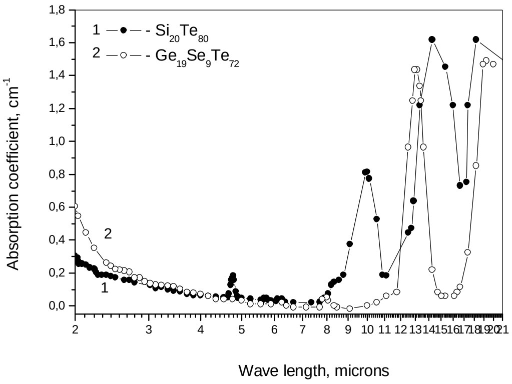

Fig. 7. Dispersion of the optical absorption coefficient of glasses: (1) $Si_{20}Te_{80}$ and (2) $Ge_{19}Te_{72}Se_9$

4. Conclusion

Thus, the comparative analysis of properties of ternary telluride Si–Ge (Ga)–Te and Si (Ge)–Te–Se glasses yielded the following results:

(i) It is shown that the basic tellurium matrix governs, to a great extent, the elastic properties of telluride glasses.

(ii) $Ge_{19}Te_{72}Se_9$ is found to be the highest quality alloy and exhibits a number of advantages in comparison to the promising acoustooptical $Si_{20}Te_{80}$ alloy studied previously [1]. Having a rather high optical homogeneity, the new alloy is more transparent, particularly in the range of the atmospheric transparency window $\lambda \sim 10–11$ μm (CO_2 laser, $\lambda = 10.6$ μm). Owing to these properties, and also because of lower acoustic attenuation, the $Ge_{19}Te_{72}Se_9$ alloy is a worthy competitor of the $Si_{20}Te_{80}$ alloy in the fabrication of modulators for the medium IR region of the spectrum.

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