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Determination of oscillator force and electronic polarizability in Fe-Sb-S-I glasses based on refractive index measurements

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The oscillator force and resonant frequencies were determined for chalcogenide glasses of $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{100-x}$ system, for x=0, 0.1, 0.5, 0.8 and 1 at % of Fe. It is noticed that resonant frequency are practically independent on iron content in investigated glasses (ω_o=9.07·10^{14} Hz). The Sellmeir dispersion formula was used to describe the dispersion characteristics of the medium. We established analytic form of the oscillator force in terms of iron content. The electronic polarizability was also determined by using Lorentz-Lorentz relation. At given wavelength of incident light the electronic polarizability decrease with increasing the density of glasses. These materials posses positive values of Grüneisen constant.

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1. Introduction

Our previously investigations of the chalcogenide materials have shown that the values of the refractive index influenced significantly on the composition of the system [1, 2]. The obtaining of amorphous samples by introducing of metal atoms impurity during the synthesis as a rule is limited to the narrow range of concentration of impurities. In the case of iron atoms this limitation varies from 0.2 at % of Fe [3] to up to 2.2 at % of Fe [4]. The implementation of Fe atoms in the chalcogenide glasses is mostly in sulfide or selenide form [5], whose para- or ferromagnetic behaviour overrules the diamagnetism of glassy matrix.

The investigations regarding the introduction of iron atoms in eutectic system of three-component Sb-S-I glass show the limit of amorphous lover than 3 at % of Fe content [6]. The investigated glasses have a wide range of transparency in IR spectra up to 20 μm [7]. The changing of the values of optical band gap is noticed at the concentration of about 1 at % of Fe. The magnetic properties show the similar behaviour: at the low concentration, proportional to Fe atom content, dominated paramagnetic arise from high spin Fe^{2+} (d^6) atoms. At the concentration upward 1 at % of Fe, the paramagnetic properties are mostly independent on impurity concentration. In the sample with 1 at % of Fe, ferromagnetic centres were formed in temperature range from 490 K to 620 K, and these could be permanent saved by fast cooling from this condition.

Up to the concentration of 1 at % Fe, DC conductivity is of semiconductor type with the activation energy about half of the value of the optical band gap, which is characteristics of the p-type conductivity of such materials [8]. The mechanism of AC conductivity is of hopping type by bipolarons between defect centres near Fermi level ($\Delta E \approx 10^{-2}$ eV). At higher Fe concentration DC and AC conductivity is of metallic type.

In this work we present the results of investigation of dispersion characteristics of refractive index at room temperature of the $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ system, and related calculated parameters. The dependence of the refraction index on the wavelength of the incident beam, in the normal dispersion range, is usually described by the Sellmeir relation [9]:

$$n^2 - 1 = \sum_i A_i \frac{\lambda^2}{\lambda^2 - \lambda_i^2} \qquad (1)$$

where the summation is carried out over the eigenvalues of the oscillator states (λ_i) of the condensed system. The value λ is the wavelength of the external electromagnetic field and the coefficient A_i is an empiric coefficient of proportionality (″oscillator force″). Parameters λ_i and A_i are strongly influenced by the structure of the material, synthesis conditions and external effects. The equation (1) could be reduced to an ordinary algebraic expression, with following assumption: only valence electrons are involved in the process and the predominant valence electrons oscillate at close, practically identical frequencies. In that case coefficient A represents the total oscillator force of the electronic system. In order to determine A and λ_o, the mentioned algebraic equation has to be linearized to the form:

$$\frac{\lambda^2}{n^2 - 1} = \frac{1}{A}\lambda^2 - \frac{1}{A}\lambda_o^2 \qquad (2)$$

There are numerous theoretical and empirical equations correlating refractive index-n (electronic polarizability α) to the density-ρ and wavelength-λ (or frequency ν_{osc}) of incident light. Usually, in all equations it is assumed that polarizability is independent of density [10]. However, in contrast to this assumption the observed functional dependence $n=n(\rho)$ indicate that polarizability is a function of frequencies, as well as of density of mater, i.e. in general case $\alpha=\alpha(\rho,\omega)$ [11]. Electronic polarizability of investigated samples was calculated using Lorentz-Lorentz equation [12]

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}\cdot N_A\cdot\alpha\cdot\frac{\rho}{M} \qquad (3)$$

where N_A is Avogadro number, M is molecular weight.

2. Experimental

The regime of synthesis $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ samples for x=0; 0.1; 0.5; 0.8 and 1 at % of Fe, was published previously [6, 7]. Because of Fe atom presence in the eutectic glass quasybinary cut of Sb_2S_3-SbI_3, the maximal temperature of synthesis was increased up to 800°C. The density of the samples was obtained by Archimedes method.

The dispersion of the refractive index, in the wavelength range from the absorption edge to 1800 nm, at room temperature, was studied on the basis of the refraction of monochromatic light beam on well-polished prisms of corresponding composition. An angle between the specially prepared prism surfaces was about 15°. The Xenon lamp XBO 450W (Osram) was the source of electromagnetic radiation and monochromatic light was obtained using SPM-2 monochromator

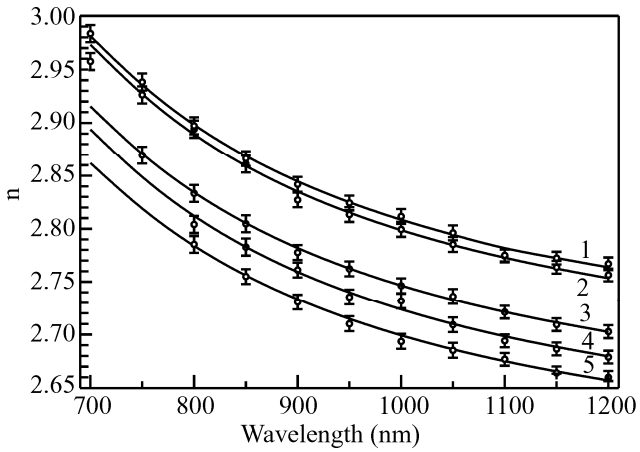

Fig 1. Dispersion of refractive index of glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ for: 1) 0; 2) 0.1; 3) 0.5; 4) 0.8 and 5) 1 at % of Fe, respectively, at room temperature.

with thermal filter and condenser optic. The incident collimated radiation was normal on prism's surface. The detector was a Si or Ge photodiode, connected to the XY plotter and moved along with horizontal axes. The scattered light intensity (i.e. the position of detected spot) was simultaneously registered at the Y-axes of the plotter.

3. Results and discussion

The measured refractive indexes of investigated glasses at room temperature are shown on Fig. 1. For given wavelength, the values of refractive index decrease almost linearly with the iron content in the glasses (Fig. 2).

The functional dependence $\lambda^2/(n^2-1)=f(\lambda^2)$ is shown on Figure 3. It is linear dependence for all investigated samples with high values of correlation coefficients between experimental results and model (0.99994-0.99998). From the parameters of the straight line one could determine A and λ_0 (with error less than 1%). Table 1. lists values of these two parameters, the energy of the oscillators (E_{osc}) and corresponding eigenfrequencies of the oscillators (ν_{osc}). The frequencies of electronic oscillators, i.e. corresponding wavelength are placed in UV part of electromagnetic spectra, which is in

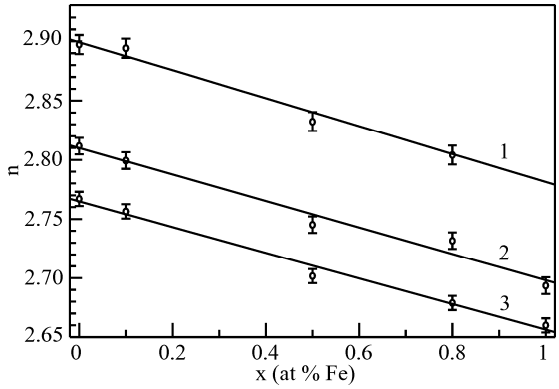

Fig. 2. Content dependence of refractive index of glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ at 1) 800 nm, 2) 1000 nm 3) 1200 nm

agreement with theoretical assumption [13]. The values of oscillator force decrease linearly with increasing of Fe concentration (Figure 4), and can be described by algebraic expression

$$A(x)=6.125-0.533\cdot x \text{ (in at \% of Fe).} \qquad (4)$$

Table 1. The experimental values of some parameters of $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ glasses.

x (at % of Fe)	ρ (kg/m3)	A	λ_o (nm)	ν_{osc} (10^{-14} Hz)	E_{osc} (eV)
0	4491.5	6.14 (2)	329.8	9.09	3.76
0.1	4492.0	6.08 (2)	332.3	9.03	3.73
0.5	4498.1	5.83 (2)	332.2	9.03	3.73
0.8	4500.8	5.70 (2)	330.6	9.07	3.75
1	4503.0	5.61 (2)	328.7	9.13	3.77

The obtained density of investigated samples and calculated values of electronic polarizability in the wavelength range from λ=800 nm to λ=1800 nm using the equation (3) are shown on Figure 5. It is noticed that electronic polarizability decreased and density increased with increasing iron content in the chosen system. At chosen frequencies of the incident light, the electronic polarizability is linearly proportional to the density of material (in agreement with the relation (13) in [11]). The fact that α (as well as n) decreased with increasing density suggests that these transparent materials posses positive values of Grüneisen constant <γ> [11].

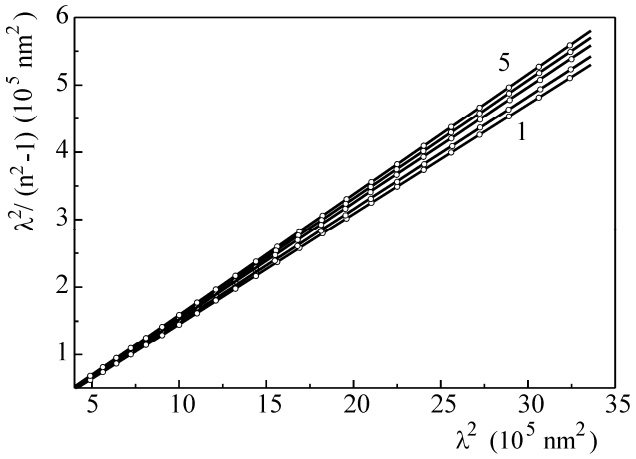

Fig. 3. Linearized dispersion function of glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ for: 1) 0; 2) 0.1; 3) 0.5; 4) 0.8 and 5) 1 at % of Fe, at room temperature.

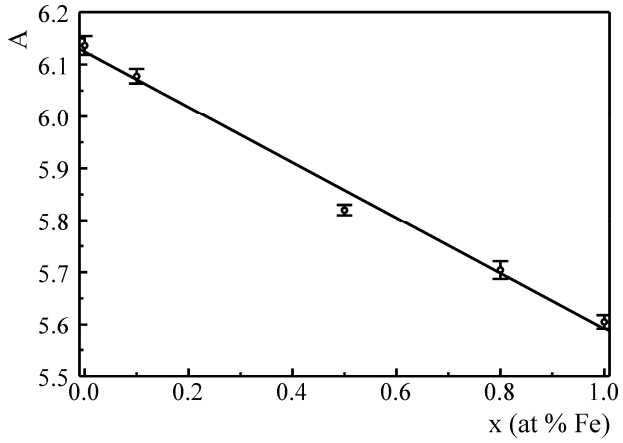

Fig. 4. Concentration dependence of oscillator forces in glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ at room temperature.

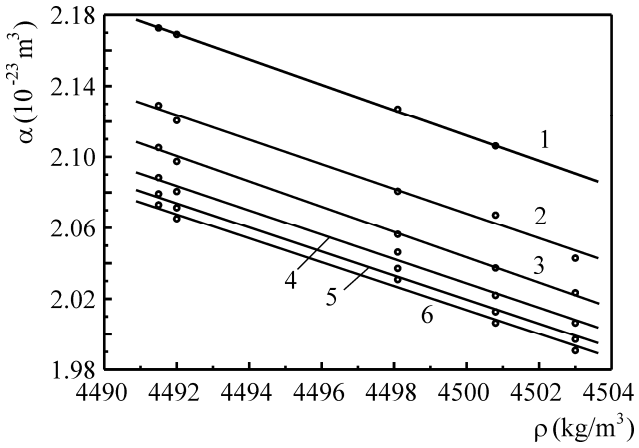

Fig. 5. Polarizability dependence on sample density in glasses $Fe_x[(Sb_2S_3)_{0.75}(SbI_3)_{0.25}]_{1-x}$ at different wavelength: 1) 800; 2) 1000; 3) 1200; 4) 1400, 5) 1600 and 6) 1800 nm.

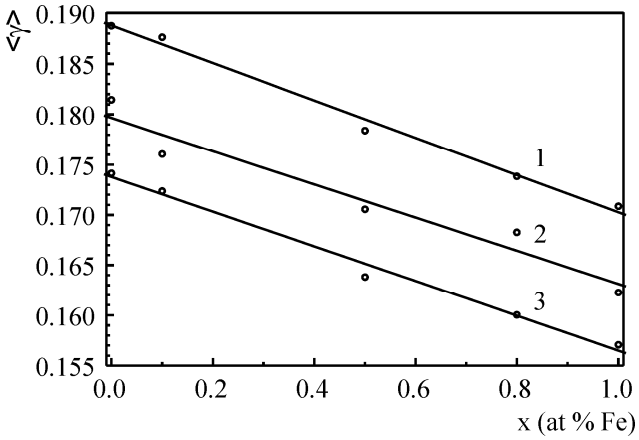

Fig. 6. The mean values of Grüneisen constant <γ> at wavelength: 800 nm; 2) 1000 nm; 3) 1200 nm.

Differentiating eq. (3) and using eq. for the polarizability α given in [14] as a function of angular frequency of incident light ω, density ρ, the mean mod Grüneisen constant <γ> could be expressed as

$$<\gamma> = \frac{2(n^2-1)(n^2+2)+6n\omega\left(\frac{\partial n}{\partial \omega}\right)_T}{(n^2-1)(n^2+2)-6n\rho\left(\frac{\partial n}{\partial \rho}\right)_T} \qquad (5)$$

The calculated values of <γ> are presented on Fig. 6 at 800, 1000 and 1200 nm.

4. Conclusion

The values of eigenfrequencies of electronic oscillators, which practically do not depend on iron content in the studied glasses, justify the use of the simplified model (relation (2)) since they prove indirectly that there exists a single type of influence to the electronic polarization. Linear dependence of oscillator force from Fe content points to uniformly dilution of Fe atoms in the glassy matrix in observed concentration range. Electronic polarizability decreased and density of glasses increased with increasing iron content and linear dependence between electron polarizability and density of the materials can be established. The calculated Grüneisen constant $<\gamma>$ as one of the important parameter for characterising and extrapolating the thermophysical properties of materials has positive values.

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