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Physical properties of vitreous As_2Se_3 doped with lead

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Influence of lead, added in metallic form, on the phase transitions, ac and dc conductivities, static permittivity, density, microhardness, and thermal diffusivity of vitreous As_2Se_3 is investigated. Concentration and temperature dependences of the physical properties are studied over the complete glass-forming region. Effect of aging at RT and annealing near T_g on the physical properties is examined. A concentration dependence of the electrical conductivity going through a distinct minimum indicates an incorporation of lead ions in the form of 4-fold coordinated cations. This type of building-in is usual for heavy metals in As_2Se_3 glasses.

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1. Introduction

Doped chalcogenide glasses have interesting electrical and optical properties and extensive applications in solid-state devices. Doping of As_2Se_3 glasses with different impurities influences not only the optical and electrical properties but also thermophysical, and mechanical properties due to structural and electronic changes of the glass network [1]. In this paper, 1/ influence of lead, added in metallic form, on the 1/ phase transitions, ac and dc conductivities, static permittivity, density, microhardness, and thermal diffusivity of vitreous As_2Se_3, and 2/ influence of an annealing below T_g or long-time aging at RT on the physical properties of the vitreous As_2Se_3:Pb are investigated. Temperature dependences of the physical properties are studied over the completely glass-forming region. The obtained results enable to appreciate glass-forming and homogeneity regions of glasses, to discuss a manner of incorporation of lead ions, and to appreciate mechanisms of electrical conduction and thermal diffusivity. To study an influence of Pb doping in chalcogenide glasses is of interest as, in glassy Ge-Se system, this doping changes the p-type conductivity to the n-type one [2-8]. Pb containing chalcogenide glasses can be used also as Pb(II)-ion-selective electrodes [9-11].

This work is a part of our complex study on the influence of impurities added in different chemical forms on physical properties of As_2Se_3 glasses [1].

2. Experimental details

Glasses were prepared by melting stoichiometric As_2Se_3 with metallic lead (0.5-5 mol %), in sealed evacuated rocking quartz ampoules, at 850 ^oC, for 10 hours. The melt was rapidly cooled (35 ^oC/min) to 300 ^oC, annealed at this temperature for 2 hours, and then slow cooled to room temperature (RT) [12, 13]. As to appreciate the stability of the glass network, several samples were annealed at 160 ^oC for 7 hours, or aged, at RT, for 2 years.

Ac conductivity and dielectric permittivity were measured over the frequency range of 100 Hz-1 MHz, at RT-180 ^oC. Relative static permittivity (ε_s) and dc conductivity (σ) were determined using the modular or impedance spectroscopy, respectively. Calculations of static permittivity using Kramers-Kronig relations were also used. Direct measurements of the dc conductivity, with a dc current, were made, at linear heating (2 ^oC/min), in the temperature range -20-160 ^oC. For electrical measurements, a "sandwich" arrangement with painted graphite or evaporated Au, Ag, and Al electrodes was used. Electrical measurements were done in vacuum or dry Ar. All measurements were repeated 10 times, under the same conditions, and the error of the calculated average value was determined. The error bars are usually smaller than dimensions of corresponding signs in figures. Mean standard errors are given in Tables 1 and 2.

The density (d) was measured, at RT, using the pycnometric method. The microhardness (H) was determined by Vickers method, at RT, upon loading with 0.65 N, for 10 s. Temperatures of glass transition (T_g, onset values), crystallization (T_x, maximum value), and melting (T_m) were determined using DTA (heating at 20 ^oC/min, in dry Ar) method. The thermal diffusivity (D_T) was measured by a pulse method, in vacuum, up to the melting temperature.

As to appreciate homogeneity of glasses and presence of crystalline inclusions the infrared (IR) and optical microscopy, and X-ray diffraction (XRD) were used, respectively.

3. Results and discussion.

In Fig.1, the influence of lead on the dc conductivity of vitreous As_2Se_3 is shown. At all concentrations of Pb, the temperature dependences of the dc conductivity (σ_{dc}) are Arrhenius-like,

$$\sigma_{dc} = \sigma_o \exp(-E_o/kT) \quad (1),$$

where σ_o is a pre-exponential factor (in chalcogenide glasses, for a band mechanism of conduction, $\sigma_o = 10^3 - 10^4$ Scm^{-1} [14-16]), E_σ is the conduction activation energy (in eV) (in chalcogenide glasses, for a band mechanism of conduction, $2E_\sigma \approx E_o$, where E_o is the optical gap), and k is the Boltzmann constant. Concentration dependences of σ_o, E_σ, and σ_{300} (dc conductivity at 300 K) are shown in Table 1. Up to 5 mol % Pb, they indicate the same type of the conductivity as in "pure" As_2Se_3 - a band character of the p-type conduction. Upon doping with 1.5 mol% Pb, a minimum conductivity is observed. Doping with Pb enables to change the conductivity of the As_2Se_3 glass over one order of magnitude. The highest Pb concentration, which gives a homogeneous glass, is equal to 5 mol% Pb. At this concentration, the conductivity is slightly higher and the activation energy is slightly lower than the corresponding values of "pure" vitreous As_2Se_3. Upon annealing for 7 hours, the dc conductivity slightly decreases; minimum conductivity is observed at 0.5 mol% Pb (Table 1). Similar changes are observed upon ageing at RT, for 2 years.

Table 1. Parameters of temperature dependences of the dc conductivity in vitreous As_2Se_3 doped with Pb: conduction activation energy, E_σ, pre-exponential factor, σ_o, dc conductivity at 300 K, σ_{300}, and static permittivity, for various concentrations of Pb.

Concentration of Pb [mol%]	E_σ [eV]	σ_o [S cm^{-1}]	$\sigma_{300}\cdot10^{12}$ [S cm^{-1}]	ε_s
0	0.877±0.03	630±70	1.1±0.1	10.56±0.09
0.5	0.898±0.03	770±90	0.7±0.1	11.52±0.09
1	0.922±0.03	1100±150	0.4±0.05	11.88±0.09
3	0.912±0.03	980±90	0.5±0.05	10.49±0.09
5	0.851±0.03	410±70	2.2±0.2	11.18±0.09
0.5 (annealed)	0.930±0.03	1500±300	0.35±0.04	10.20±0.2
1 (annealed)	0.915±0.03	1200±250	0.5±0.05	10.00±0.2
3 (annealed)	0.903±0.03	750±90	0.5±0.05	7.43±0.06
5 (annealed)	0.851±0.03	370±70	2±0.2	8.90±0.07

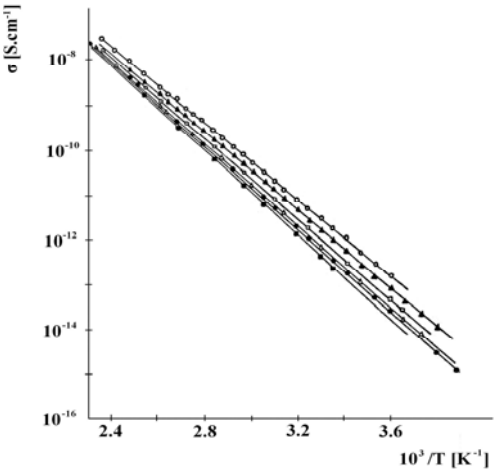

Fig.1. Temperature dependences of the dc conductivity of glassy As_2Se_3 doped with Pb (▲▲▲ 0, ´ 0.5, ●●● 1, ■■■ 1.5, ΔΔΔ 3, ooo 5 mol% Pb)

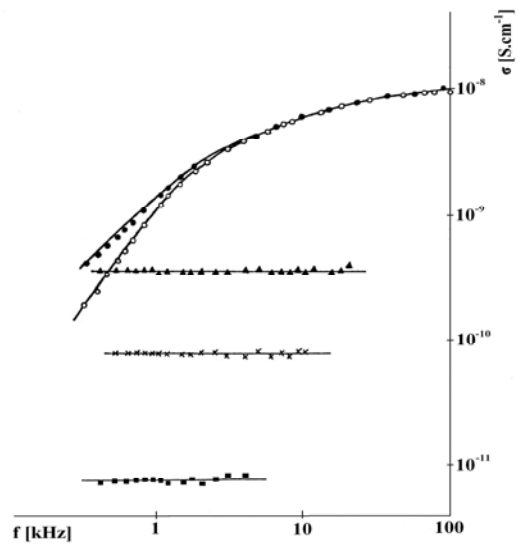

Fig. 2. Frequency dependences of the ac conductivity in fresh and annealed glassy As_2Se_3:3 mol% Pb, at various temperatures (fresh samples: ■■■ 42 °C, xxx 69 °C, ▲▲▲ 90 °C; annealed samples: ooo 46 °C, ●●● 82 °C).

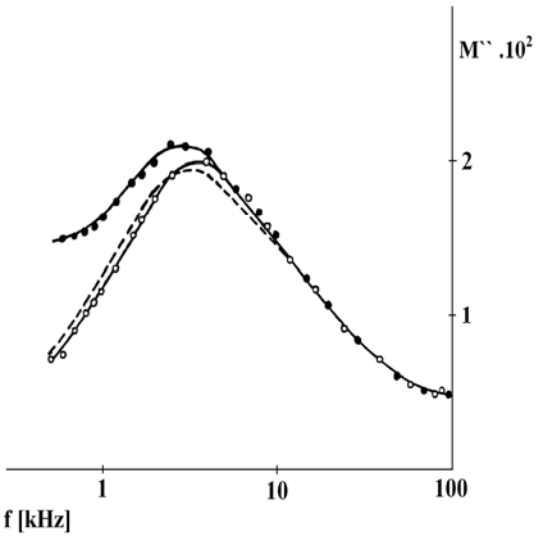

Fig. 3. Frequency dependences of the imaginary part of the electrical modulus in annealed glassy As_2Se_3:3 mol% Pb, at various temperatures (ooo 46 °C, ●●● 82 °C, dashed line represents Debye maximum)

The ac conductivity of "fresh" samples, up to 100 kHz, is independent of the frequency and is equal to the dc conductivity (Fig. 2). It means that doping with Pb significantly decreases the ac component, $\sigma_{\sim}$, of the conductivity (in "pure" As_2Se_3, $\sigma_{\sim} = 5\cdot10^{-12} f^{0.88\pm0.08}$, where f is the frequency in kHz). Up to now, this component was supposed to be almost independent of the glass composition or doping [1,17]. However, in As_2Se_3 glasses, we have observed an increase of this component for traces of H_2Se or O_2, and upon doping with U or Al. Usually, the temperature dependence of this component is negligible

[1, 16]. Upon annealing, an intensive dielectric relaxation appears in glasses doped with 3 or 5 m/o Pb (Fig. 3). The ac component of the conductivity increases, almost independently of the temperature (Fig. 2).

The frequency dependence of the imaginary part of the complex electrical modulus [18], M'', has a maximum in the range of 3-8 kHz;

$$M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2) \quad (1),$$

where ε' and ε'' are the real and imaginary parts of the permittivity. The activation energy of this relaxation is low (≤ 0.08 eV) (Figs. 2, 3). The large dielectric maximum is Debye-like. Its intensity increases with increasing concentration of Pb. At 5 mol% Pb, another type of relaxation appears in "fresh" glasses – a maximum below 0.5 kHz with the activation energy of 0.47 eV. A small side-maximum of this type is observed also in annealed glasses doped with 3 or 5 mol% Pb (Fig. 4). This side-maximum corresponds to a broad dielectric relaxation. Both dielectric dispersions come from the Maxwell-Wagner relaxation in inhomogeneous dielectrics [19]. However, the structure and composition of separated, PbSe richer phases, which are induced by melting (in heavily doped fresh samples) or by annealing below T_g, are different.

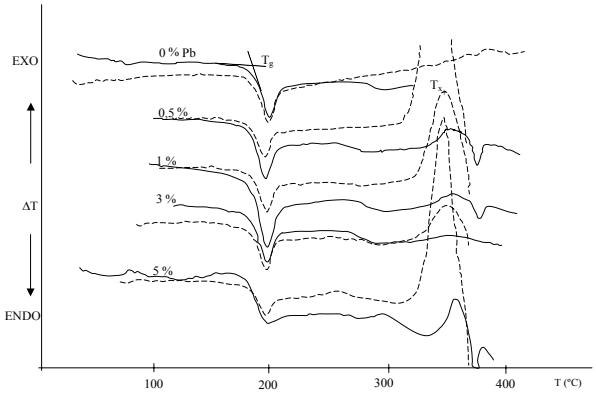

Fig. 4. DTA plots of vitreous As_2Se_3 doped with 0 - 5 mol% Pb ("fresh" samples - full lines, annealed samples – dashed lines)).

Below T_g, the frequency and temperature dependences of the permittivity are negligible [20] and the measured values are equal to the static permittivity, ε_s. At T_g, the static permittivity significantly decreases due to a structural relaxation of glasses [21, 22]. Values of the static relative permittivity, ε_s, are shown in Table 1. In phase-separated glasses, the static permittivity decreases. This decrease is more pronounced when the phase separation results from annealing below T_g.

Upon doping with Pb, the microhardness increases (Table 2). It is a typical impurity hardening, which is characteristic for doped As_2Se_3 glasses [1, 16]. At doping with 5 mol% Pb, phase separation enhances the impurity hardening. Because the microhardness is a function of the strength of individual bonds and the atomic packing density, in vitreous Ge-Se system, the microhardness decreases with the addition of Pb [23].

A decrease of the density with increasing concentration of heavy Pb ions (Table 2) is unusual. It supports the supposition on building-in of Pb^{2+} ions between As_2Se_3 layers using coordination bonds [27]. This type of sewing-together of layers is usual at doping with heavy metals [1, 16, 24-26]. This incorporation of large Pb^{2+} ions results in expansion of the glass network.

In "pure" As_2Se_3 (both fresh and annealed), T_g = 182±1 °C and neither crystallization nor melting can be detected. Glasses are very pure and do not contain germs of crystallization. Pb doping induces both crystallization and melting of glasses (Fig. 4). Annealing below T_g results in a decrease of both T_x and T_{cr}, and in enhancement of the entropy of both transitions (Table 2). Separated clusters, rich on PbSe, form effective nucleation centers and act catalytic on both crystallization and melting. A single crystallization process at 354 ± 2 °C (T_x) and melting at 375 ± 3 °C (T_m) are observed (Table 2). Upon annealing near T_g, the value of T_x decreases to 344 ± 5 °C.

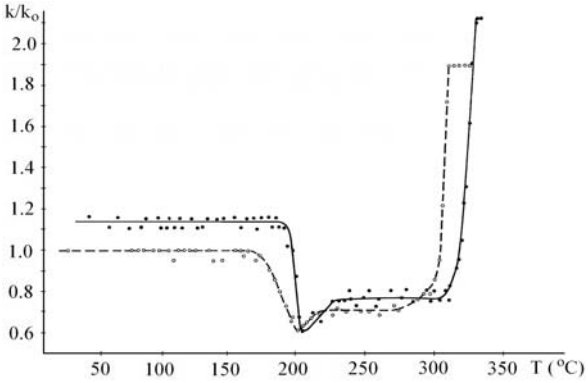

Fig. 5. Temperature dependence of the thermal diffusivity of vitreous As_2Se_3:5 mol% Pb (full line – "fresh sample", dashed line – annealed samples).

Table 2. Microhardness, H, density, d, glass transition temperature, T_g, crystallization temperature, T_x, and melting temperature, T_m, in vitreous As_2Se_3 doped with Pb.

Concentration of Pb [mol%]	H [N/mm^2]	d [g/cm^3]	T_g [^{o}C]	T_x [^{o}C]	T_m [^{o}C]
0	1490±10	4.59±0.02	183±1	---	373±2
0.5	1540±10	4.39±0.02	182±1	353±2	374±2
1	1500±10	4.59±0.02	183±1	354±2	376±2
3	1530±10	4.26±0.02	184±1	354±2	378±2
5	1620±20	4.36±0.02	180±1	356±2	372±2
0.5 (annealed)	---	---	182±1	338±2	372±2
1 (annealed)	---	---	183±1	345±2	374±2
3 (annealed)	---	---	185±1	349±2	374±2
5 (annealed)	---	---	182±1	345±2	373±2

We have studied phase transitions also by measurements of thermal diffusivity (Fig. 5). A typical temperature dependence of the thermal diffusivity of vitreous As_2Se_3 doped with Pb is shown in Fig. 3. Because thermal diffusivities of the glass, undercooled liquid, and crystal are significantly different (in As_2Se_3:5 m/o Pb, D_T(glass) = $1.3\cdot10^{-3}$ cm^2/s, D_T(liquid) = $9\cdot10^{-4}$ cm^2/s, D_T(crystal) = $2.5\cdot10^{-3}$ cm^2/s) both T_g and T_x can be determined by this technique. Upon annealing, the glass transition is smeared, and both T_g and T_x decrease. Up to T_g, thermal diffusivity is almost temperature independent. Above T_g, D_T decreases due to structural relaxation and increasing disordering of undercooled liquid. Upon crystallization, D_T significantly increases due to formation of an ordered lattice.

4. Conclusions

Vitreous As_2Se_3 can be homogeneously doped with Pb up to 5 mol%; upon a 7 hour's annealing near T_g, a phase separation is observed in glasses containing 3 and 5 mol% Pb. Up to 5 mol% Pb, no crystalline inclusions are observed.

In glassy As_2Se_3, the concentration dependence of the dc conductivity goes through a shallow minimum at 1 mol% Pb. It points out structural changes in the glass network, upon doping with Pb. A minimum in the concentration dependence of the dc conductivity is typical for incorporation of heavy metals, in this case Pb, as a 4-fold coordinated cation using coordination bonds [27]. Temperature and frequency dependences of the dc and ac conductivities show that the dc conductivity has a band character of conduction. Upon doping with Pb, the ac component of the conductivity is suppressed.

Upon doping with heavy Pb, a decrease of the density indicates structural expansion of the glass network; lead ions probably enter between As_2Se_3 layers.

Upon annealing, structural changes and phase separation result in a decrease of the static permittivity.

Doping with Pb brings about an impurity hardening. The hardening is most significant in phase separated "fresh" glass containing 5 mol% Pb.

In "pure" As_2Se_3 (both fresh and annealed), T_g = 182±1 ^{o}C, and neither crystallization nor melting can be detected. Glasses do not contain germs of crystallization. Pb doping induces both crystallization and melting of glasses. In doped glasses, a single crystallization process at 354 ± 2 ^{o}C (T_x) and melting at 375 ± 3 ^{o}C (T_m) are observed. Upon annealing near T_g, the value of T_x decreases to 344 ± 5 ^{o}C.

In glasses, thermal diffusivities of the glass, undercooled liquid, and crystal are significantly different (e.g. in As_2Se_3:5 m/o Pb, D_T(glass) = $1.3\cdot10^{-3}$ cm^2/s, D_T(liquid) = $9\cdot10^{-4}$ cm^2/s, D_T(crystal) = $2.5\cdot10^{-3}$ cm^2/s). Upon annealing, the glass transition is smeared, and both T_g and T_x decrease. Up to T_g, thermal diffusivity is temperature independent. Above T_g, D_T decreases due to structural relaxation and due to increasing disordering of undercooled liquid. Upon crystallization, D_T significantly increases due to formation of an ordered lattice.

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