JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 12, December 2009, p. 2058 - 2062

Electrical and dielectric properties of As-Se glasses doped with uranium

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Influence of uranium, added in metallic form, on the density, glass transition temperature, ac and dc conductivities, and static permittivity of vitreous As_2Se_3, $As_2Se_{7.9}$, and Se is investigated. Concentration and temperature dependences of the physical properties are studied over the whole glass-forming region. In glassy As_2Se_3, heavy metals are usually incorporated as 4-fold coordinated cations. Therefore, the concentration dependence of the electrical conductivity goes through a minimum. At high concentrations of U (≥0.5 mol%), high conductivities are observed. A distinct minimum of both the static permittivity (at 0.1 mol% U, it decreases by 25 %) and dc conductivity (at 0.2 mol% U, it decreases by 10^{-3} times), at low concentrations of U, reflects an extraordinary electrical activity of this impurity in vitreous As_2Se_3. Enlargement of glass forming regions in As-Se-U system with increasing Se:As ratio was not confirmed.

(Received July 5, 2009; accepted November 12, 2009)

Keywords: Chalcogenide glasses, As_2Se_3; $As_2Se_{7.9}$; Se, Doping with U, ac conductivity, dc conductivity, density; T_g, Static permittivity

1. Introduction

Doped chalcogenide glasses are interesting materials for electrical and optical applications. Doping of As_2Se_3 glasses with different impurities influences not only the optical but also electrical and mechanical properties due to structural and electronic changes of the glass network [1]. In this paper, an influence of uranium, added in metallic form, on the density, glass transition temperature, ac and dc conductivities, static permittivity and glass-forming region of vitreous As_2Se_3, $As_2Se_{7.9}$, and Se is reported. Temperature dependences of the physical properties are studied over the whole glass-forming region but the main attention is paid to low concentrations of uranium. The obtained results enable to appreciate glass forming and homogeneity regions of glasses, and to discuss the manner of incorporation of uranium ions. This work is a part of our complex study on the influence of impurities added in different chemical forms on physical properties of As-Se glasses [1].

2. Experimental details

Glasses were prepared by melting stoichiometric As_2Se_3, non-stoichiometric $As_2Se_{7.9}$, or pure Se with a chosen amount of metallic uranium (0.05-1 mol%), in sealed evacuated rocking quartz ampoules, at 960 °C, for 10 hours. The melt was rapidly cooled (35 °C/min) to room temperature (RT) or LNT [2]. As to appreciate the stability of the glass network, some samples were annealed at 160 °C for 7 hours.

Temperatures of glass transition (T_g, onset values) were determined using DTA (heating rate of 5-20 °C/min). Relative static permittivity (ε_s) and dc conductivity (σ) (5 Hz-10 MHz, LNT-180 °C) were determined using the modular or impedance spectroscopy, respectively. Also direct measurements of the dc conductivity were made, at linear heating (2 °C/min), and calculations of static permittivity using Kramers-Kronig relations were used. All measurements were repeated 10 times, under the same conditions, and the error of the calculated average value was determined. Error bars are usually smaller than dimensions of corresponding signs in figures. Mean standard errors are given in Tables 1-3.

As to appreciate homogeneity of glasses and occurrence of crystalline inclusions the infrared (IR) or optical microscopy and X-ray diffraction (XRD) were used, respectively. At 0.5 and 1 mol% U, IR microscopy shows phase separation. At 2 mol% U, XRD shows crystalline inclusions.

3. Results and discussion

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

$$\sigma_{dc} = \sigma_o \exp(-E_\sigma/kT) \qquad (1)$$

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} [1,3,4]), 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 Boltzman constant. Concentration dependences of σ_o, E_σ, and σ_{300} (dc conductivity at 300 K) are shown in Table 1. In “pure” As_2Se_3, the ratio of E_σ/E_o, is equal to 0.56 [1].

Upon doping, up to 0.2 mol% U, this ratio slightly decreases. At higher concentrations, this decrease is very abrupt. It indicates a band character of conduction only at low concentrations of U. Doping with U influences dc conductivity of glassy As_2Se_3 remarkably. Doping with 0.1 mol% U brings about a drop of the dc conductivity by more than two orders of magnitude, at RT. For 0.2 mol% U, the dc conductivity approaches to that of the pure As_2Se_3. At this concentration, the ac component of the conductivity increases appreciably and the slope of its frequency dependence changes to a value typical for a non-homogeneous glass (Fig. 2). At room temperature, at the same concentration, 0.2 mol% U, a side maximum in the modular spectrum [5] appears (at RT, its position is near 4 kHz), upon an annealing at 160 °C for 7 hours. The position of this peak is temperature activated with activation energy of 0.51 eV. This value is close to that of the conduction activation energy of glasses containing 0.5 mol% U (Fig.2). This side-maximum corresponds to a broad spectrum of dielectric relaxation times. Both phenomena indicate that more conducting micro-regions (containing a higher concentration of U) are dispersed in the high resistive vitreous As_2Se_3 doped with a smaller amount of U. Maxwell-Wagner-Szillars theory on inhomogeneous dielectrics must be applied [6]. Up to 0.2 mol% U, IR microscopy or XRD does not show inhomogeneities or crystalline inclusions. Thus, electrical methods react more sensitively on electrical or dielectric inhomogeneities.

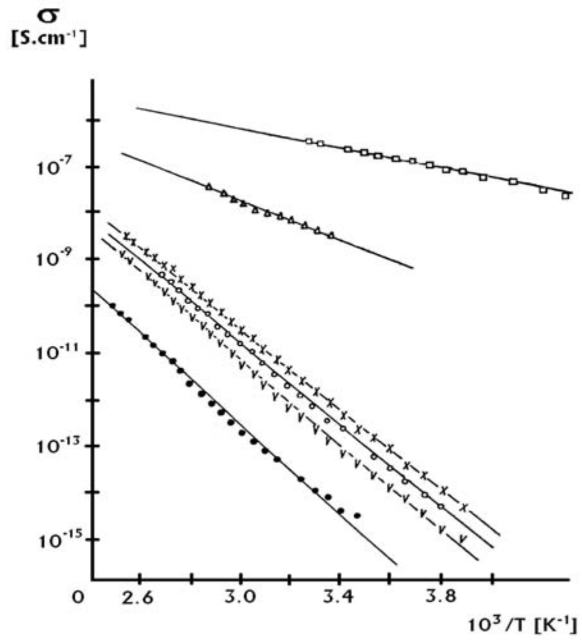

Fig. 1. Temperature dependences of the dc conductivity of glassy As_2Se_3 doped with U (xxx 0, vvv 0.05, ●●● 0.1, ooo 0.2, ΔΔΔ 0.5, □□□ 1 mol% U).

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

Concentration of U [mol% U]	E_σ [eV]	σ_o [S cm^{-1}]	σ_{300} [S cm^{-1}]
0	0.87±0.01	500±100	(1.3±0.1)x10^{-12}
0.05	0.92±0.01	530±100	(2.2±0.2)x10^{-13}
0.1	1.04±0.01	740±150	(8±0.7)x10^{-15}
0.2	0.91±0.01	1055±200	(5±0.6)x10^{-13}
0.5	0.41±0.01	(3±0.7)x10^{-2}	(4±0.4)x10^{-9}
1	0.21±0.01	(1±0.2)x10^{-3}	(4±0.4)x10^{-7}

At 0.5 and 1 mol% U, dc conductivity significantly increases and its activation energy significantly decreases. Optical and IR microscopy shows a phase separation. However, low activation energies indicate the presence of a crystalline phase. Probably, our samples are glass-crystalline, at these concentrations of U.

The total ac conductivity, σ_{ac}, is composed from the dc conductivity, σ_{dc}, and from an ac component, $\sigma_\sim$. The frequency dependence of this component is power-like, $\sigma_\sim = A f^s$ (Fig. 3) [1,4,8-10]. Therefore,

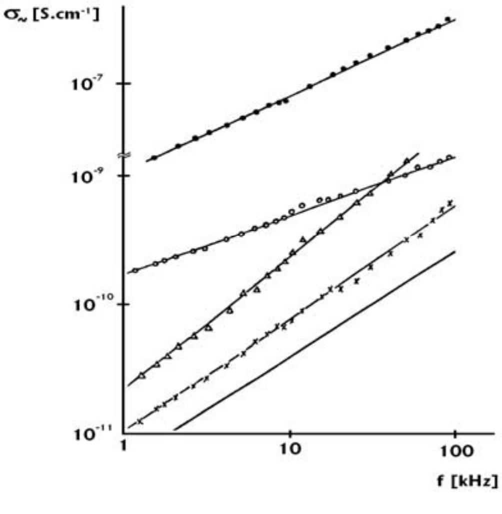

Fig. 2. Frequency dependences of the ac component, $\sigma_\sim$, of conductivity in glassy As_2Se_3 doped with U (full line – 0, xxx 0.05, ΔΔΔ 0.1, ooo 0.2, ●●● 1 mol% U)

$$\sigma_{ac} = \sigma_{dc} + A f^{s} \qquad (3)$$

where σ_{ac} and σ_{dc} are ac or dc conductivities in Scm^{-1}, respectively, f is frequency in kHz, and A is almost independent of temperature. Due to a low dc conductivity of glassy As_2Se_3 doped with U (up to 0.2 mol%), determination of the ac component is very reliable. Up to 0.2 mol% U, a contribution of σ_{dc} to σ_{ac}, near RT, is negligible. As in other doped As_2Se_3 glasses [1], the value of s is equal to 0.9±0.1, for homogeneous glasses, and to

0.5±0.1, for phase separated glasses. It indicates a phase separation, for concentrations of U ≥ 0.2. Up to 0.1 mol% U, the ac component of the conductivity could be explained by a phonon-assisted pair-hopping mechanism at Fermi level [3,7]. Using this model, a density of states at Fermi level, $N(E_F)$, could be approximately calculated from $\sigma_{\sim}$. For 300 K, phonon frequency 10^{12} Hz, electrical field frequency 0.642 kHz, an approximate equation [8] is valid,

$$[N(E_F)]^2 = 6.4 \cdot 10^{49}\, \sigma_{\sim}(f)\, \alpha^5 \qquad (4)$$

where, for chalcogenide glasses, $\alpha^{-1} \cong 0.8$ nm. Upon doping, the density of states increases from $3 \cdot 10^{18}$ (pure As_2Se_3) to $5 \cdot 10^{19}$ cm^{-3} eV^{-1} (0.1 m/o U). These values are reasonable, as for chalcogenide glasses $N(E_F)$ values usually range between 10^{18} and 10^{21} cm^{-3} eV^{-1} [3]. At higher concentrations of U, the calculated $N(E_F)$ abruptly decreases indicating another mechanism of the ac component. However, this model requires a decrease of s with increasing frequency, s ≤0.85, and a linear temperature dependence of $\sigma_{\sim}$. These features were not experimentally confirmed. Elliott's model [9, 10] for hopping of bipolarons over a correlated barrier requires a temperature dependence of $\sigma_{\sim}$ which was not observed. Therefore, Jonscher's universal model of dielectric response is most probable [11]. However, the value of $\sigma_{\sim}$ depends on the concentration of U, also in the concentration region of homogeneous glasses. Thus, observation of the universal value of $\sigma_{\sim}$ for chalcogenide glasses [1,12] is not valid for U doped glasses.

Up to 0.2 mol% U, the frequency and temperature dependences of permittivity are negligible and the measured values are equal to ε_s. At T_g, static permittivity significantly decreases due to structural relaxation of glasses [13,14]. Values of the static relative permittivity, ε_s, are shown in Table 2. The relation

$$\varepsilon(f) = \varepsilon_s + 1.8 \cdot 10^9 \cdot \sigma_{\sim}(f) \cdot f^{-1} \cdot \mathrm{tg}\,(\pi s/2) \qquad (5)$$

determines the frequency dependence of the relative permittivity. In the frequency region where $\sigma_{\sim}(f) = A\, f^{\,s}$, the relation

$$\varepsilon(f) = \varepsilon_s + \varepsilon(1) \cdot f^{\,s-1} \qquad (6)$$

is valid. In both equations, the frequency is in kHz. For 0.2 and 1 mol% U, the equation (6) was used for calculation of ε_s. The values were confirmed by the modular spectroscopy. As the static permittivity is influenced also indirectly through a change of density, d, by doping, a reduced relative permittivity [15],

$$\varepsilon_r = (\varepsilon_s - 1)/d \qquad (7)$$

is also calculated. Thus, the influence of changes in density on the concentration dependence of the reduced permittivity is eliminated.

Distinct minima of the dc conductivity and static permittivity at 0.1 mol% U reflect an extraordinary intensive electrical activity of this impurity. Such minima are usually met upon doping with heavy metals (Hg, Pb, Cu) [1, 15-17], which are incorporated into a glass-network as 4-fold coordinated cations using coordination bonds [18].

Table 2. Static relative permittivity, ε_s, reduced relative permittivity, ε_r, density, d, at RT, power exponent, s, and glass transition temperature, T_g, in vitreous As_2Se_3 doped with U

Concentration of U [mol%]	ε_s	ε_r [cm^3/g]	d [g/cm^3]	s	T_g [°C]
0	10.5±0.2	2.26	4.64±0.02	0.8±0.05	181±1
0.05	10.1±0.2	2.19	4.61±0.02	0.88±0.05	175±1
0.1	9.0±0.3	2.08	4.47±0.02	1.0±0.05	173±1
0.2	10.5±0.2	2.25	4.66±0.02	0.44±0.05	183±1
1	11.4±0.2	2.45	4.65±0.02	0.57±0.05	184±1

Table 3. Conduction activation energy, E_σ, pre-exponential factor, σ_o, dc conductivity at 300 K, σ_{300}, power exponent, s, relative static permittivity, ε_s, and glass transition temperature, T_g, in vitreous $As_2Se_{7.8}$ or Se doped with U, for various concentrations of U.

glass	E_σ (eV)	σ_o (S cm^{-1})	σ_{300} (S cm^{-1})	s	ε_s	T_g (°C)
$As_2Se_{7..9}$ – „pure“	0.91	$2.4x10^3$	$7x10^{-13}$	1.00	10.9	126
$As_2Se_{7..9}$: 0.1 mol% U	0.86	396	$1.4x10^{-12}$	0.80	11.2	124
$As_2Se_{7..9}$: 0.5 mol% U	0.30	$2.2x10^{-3}$	$1.8x10^{-8}$	0.65	11.0	127
$As_2Se_{7..9}$: 1 mol% U	0.25	$2.8x \cdot 10^{-3}$	$2x10^{-7}$	0.54	11.0	129
Se – „pure“	0.60	$3x10^{-4}$	$2x10^{-14}$	0.79	5.7	44
Se: 0.1 mol% U (RT)	0.20	$2.4x10^{-4}$	$1.0x10^{-7}$	0.75	6.0	46
Se: 0.5 mol% U (RT)	0.19	$3.8x10^{-4}$	$2.6x10^{-7}$	0.62	6.0	46
Se: 0.1 mol% U (LNT)	0.25	$2.9x10^{-4}$	$1.2x10^{-8}$	0.66	6.2	45
Se: 0.5 mol% U (LNT)	0.18	$5x10^{-5}$	$3x10^{-8}$	0.73	6.9	48

Note: RT means glasses cooled to room temperature, LNT means glasses quenched to LNT.

Supposing that the solubility of U increases with increasing Se/As ratio, we prepared also glassy $As_2Se_{7.9}$ and Se doped with U. In Figs. 3 and 4, we can see temperature dependences of the dc conductivity, σ, for both types of glasses. In Figs. 5 and 6, we can see frequency dependences of the ac component, $\sigma_\sim$, of the conductivity for both types of glasses, at RT. Both an extremely large increase of dc conductivities and significant decrease of their activation energies, E_σ, upon doping, show that, at 0.1 mol% U, both types of glasses are glass-crystalline (Table 3). This fact is supported by a decrease of the power exponent, s, of frequency dependences of the ac component, $\sigma_\sim$, of the conductivity for both types of glasses. It means that increasing Se:As ratio cannot enhance solubility of U. Quenching of doped Se glasses to LNT decreases the degree of crystallinity. It confirms their much lower dc conductivity than that of doped Se glasses cooled to RT.

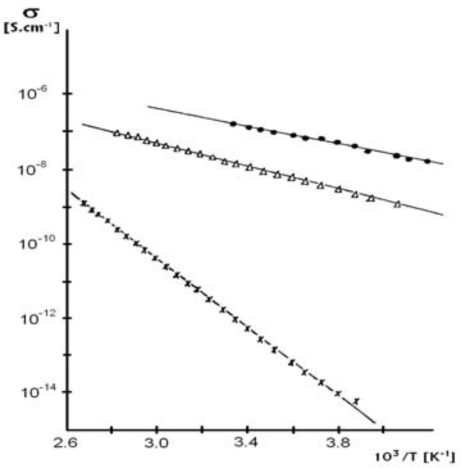

Fig. 3. Temperature dependences of the dc conductivity of vitreous $As_2Se_{7.9}$ doped with U (xxx 0, ΔΔΔ 0.5, ●●● 1 mol% U)

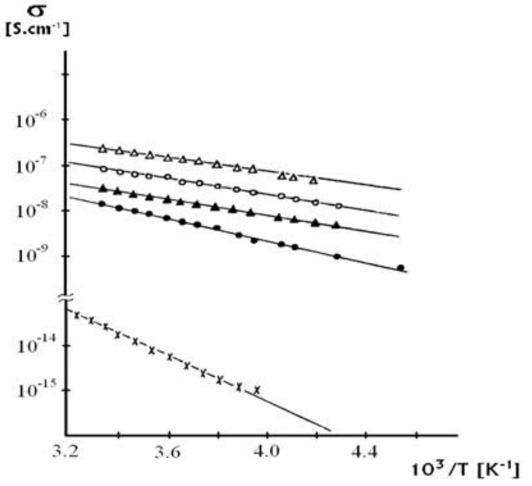

Fig. 4. Temperature dependences of the electrical conductivity of vitreous Se doped with U (xxx 0, ooo 0.5, ΔΔΔ 1 mol% U; full and empty signs are for samples quenched to RT or LNT, respectively)

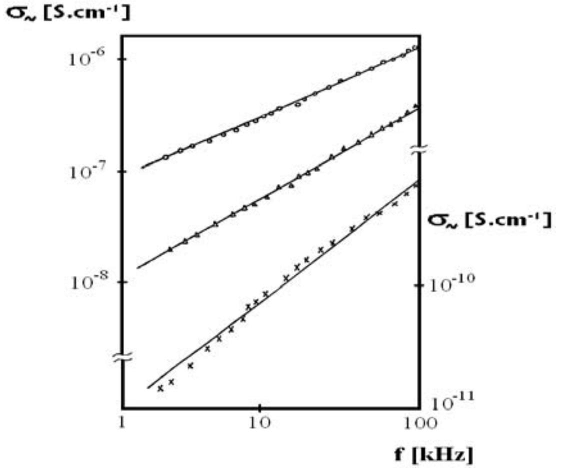

*Fig. 5. Frequency dependences of the ac component of conductivity in glassy $As_2Se_{7.9}$ doped with U (*xxx *0, ΔΔΔ 0.5,* ooo *1 mol% U).*

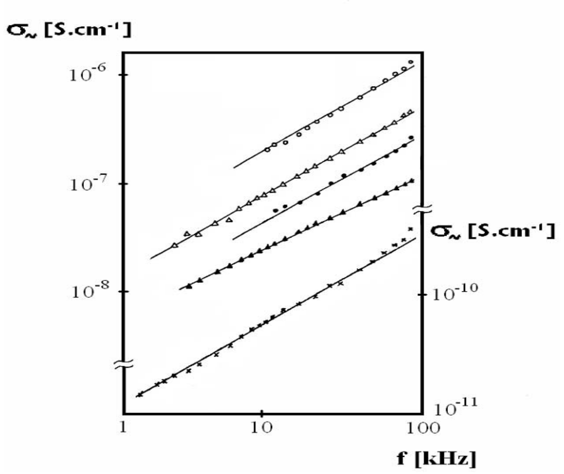

*Fig. 6. Frequency dependences of the ac component of conductivity in glassy Se doped with U (*xxx *0, ΔΔΔ 0.5,* ooo *1 mol% U; full and empty signs indicate glasses quenched to RT or LNT, respectively)*

4. Conclusions

Vitreous As_2Se_3 can be homogeneously doped with U up to 0.2 mol%; upon a long annealing near T_g, a phase separation is observed already in glasses containing 0.2 mol% U. At 0.5 and 1 mol% U, samples are glass-crystalline. Enhancement of the Se:As ratio does not enlarge the glass-forming region of As-Se-U glasses. A glass-crystalline $As_2Se_{7.9}$ occurs already at 0.5 mol% U; a glass-crystalline Se occurs already at 0.1 mol% U. A degree of crystallinity is possible to reduce by quenching to LNT. In glassy As_2Se_3, concentration dependences of T_g, density, static permittivity, and dc conductivity go through a deep minimum at 0.1 mol% U. It points out serious structural changes in the glass network, upon doping with low concentrations of U. A decrease of the density, at low concentrations of uranium, indicates structural expansion; uranium probably enters between As_2Se_3 layers. This type of incorporation results in a decrease of the static permittivity. A minimum in the concentration dependence of the dc conductivity is typical for incorporation of heavy metals, in this case U, as 4-fold coordinated cations using coordination bonds. For excessive Se, in glassy $As_2Se_{7.9}$ and Se, we do not observe such minima what indicates that these glasses are able to adapt their structure to this heavy metal in much simpler manner. However, the glass-forming region is not enlarged.

Temperature and frequency dependences of the dc and ac conductivities show that, at low concentrations of uranium (up to 0.2 mol% U in As_2Se_3, up to 0.1 mol% U in $As_2Se_{7.9}$), the dc conductivity has a band character of conduction. The ac component of the conductivity can be explained by Jonscher's universal model of dielectric response. Doping As_2Se_3 with 0.1 mol% U brings about a drop of the dc conductivity by more than two orders of magnitude, at RT. At the same time, a drop of static permittivity by 12 % is observed. It means that uranium is extremely electrically and dielectrically active in glassy As_2Se_3.

In vitreous $As_2Se_{7.9}$, and Se, we have not seen any minima in concentration dependences of the physical properties. It seems that excess of Se enables a simpler incorporation of U into the glass network. However, the glass-forming region is not enlarged.

Acknowledgement

The Scientific Grant Agency VEGA, Slovak Republic, grant project 1/0173/08, supported this work.

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