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THERMAL STABILITY AND KINETICS OF STRUCTURAL TRANSFORMATIONS IN VITREOUS CHALCOGENIDE SEMICONDUCTORS As_xSe_{100-x} AS STUDIED BY DIFFERENTIAL THERMAL ANALYSIS AND EXOELECTRON EMISSION METHODS

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Kinetics of phase transitions in γ-irradiated and non-irradiated chalcogenide glasses As_xSe_{100-x} (x = 10, 20 and 30) has been investigated by parallel differential thermal analysis (DTA) and exoelectron emission (EEE) measurements. Activation energies for the retrification process in investigated materials have been determined by the Ozawa method. It has been found that the activation energy for retrification process in the surface layers is smaller than that for the retrification in the volume. Gamma-irradiation improves the thermal stability of investigated materials.

Key words: chalcogenide glasses, DTA, exoelectron emission, activation energy, retrification, γ-irradiation.

Vitreous chalcogenide semiconductors, obtained by melting together the elements from the IV and V group of the periodic table of the elements with chalcogens (S, Se, Te), remain to be a subject of intensive investigations because of unusual combination of their physical properties. The most stimulating factor for these studies steams from potential applications of these materials, e.g. in optoelectronics [1]. These promising applications of chalcogenide glasses are, however, limited by their structural instability, resulting from the production process, in which the liquid phase is quenched to the ambient temperature [2]. The process of thermal ageing of the as-quenched material (e.g. long-lasting isothermal ageing at proper temperature) leads to the achievement of the metastable state characteristic of the overcooled liquid [1].

The ageing process of chalcogenide glasses can be stimulated by γ-irradiation [3–6,15–16]. The effect of irradiation is an additional factor complicating the control of production of materials with desired (prognozed) properties.

Amorphous materials tend to crystallize at a proper combination of temperature and time. The stability of the chalcogenide glasses may be characterized by the activation energies and temperature of the thermally activated retrification and crystallization processes. There is an additional complicating factor caused by the fact, that the parameters determining the thermal stability of the volume and of the surface

layer of amorphous materials may differ among themselves. About 20 years ago we elaborated a method [7] for determination of the thermal stability for both the surface and volume of amorphous materials by parallel measurements of the temperature dependencies of the DTA signal and the intensity of photostimulated EEE. This method has been already successfully applied in investigations of the kinetics of phase transformations in some chalcogenide glasses [8, 9] and in amorphous selenium [10].

The aim of the present communication is to report the results of investigations of the kinetics of phase transformations and of the thermal stability of chalcogenide glasses As_xSe_{100-x} (x = 10, 20 and 30) as well as the effect of γ-irradiation on these processes and their parameters.

The vitreous samples of As_xSe_{100-x} (x = 10, 20 and 30) chalcogenide glasses were prepared by the melt quenching method using a mixture of high purity precursors sealed in evacuated quartz ampoules (~10^{-3} Pa). The furnace was rocked to obtain homogeneous melt. The ingot was quenched at the ambient temperature and then annealed additionally near T_g point to remove the residual mechanical stresses. The amorphous state of chalcogenide glasses was controlled by a visible character of cinch-like fracture, data of X-ray diffraction analysis and transmission IR microscopy.

The DTA and EEE measurements were performed for two different types of samples: *a* – for samples not submitted to any excitation (irradiation) prior to measurements, and *b* – for γ-irradiated samples (Co^{60} source, energy of γ quanta 1,25 MeV, dose 2,06 MGy).

Measurements of the temperature dependencies of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [11]. An open air point counter with saturated ethanol quenching vapor was used for detecting the exoelectrons. The sample temperature, controlled using an Ni-CrNi thermocouple with an accuracy of about 5 K, was changed at four constant heating rates (2, 5, 10 and 20 K/min). The sample surface was irradiated during the measurements by unfiltered radiation from a quartz lamp with a Q-400 burner.

The calorimetric investigations of the volume retrification were performed at five heating rates (1, 2, 5, 10 and 20 K/min) using the NETZSCH DSC 404/3/F differential calorimeter with E-type thermocouple using an empty crucible made of high density Al_2O_3 as references. All the EEE and DTA measurements were performed in air under ambient pressure.

Temperature dependencies of the intensity of photostimulated exoelectron emission (EEE) and of the differential thermal analysis signal (DTA), from non-irradiated (a) and γ- irradiated (b) chalcogenide glasses As_xSe_{100-x}, all measured at the same heating rate of 5 K/min. are shown in fig. 1. The parameter of the curves presented in this figure is the arsenic content (x) in the sample. The temperature dependencies of the intensity of exoelectron emission presented in fig. 1 display a maximum coinciding with the endothermal effect occurring on the DTA curves. The temperatures of these anomalies occurring on both the EEE and DTA curves systematically increase with increasing of the arsenic content in investigated samples. The process responsible for the effects displayed by EEE (surface sensitive method) and DTA (volume sensitive method) is the retrification process occurring in the surface layer and in the volume of investigated sample, correspondingly.

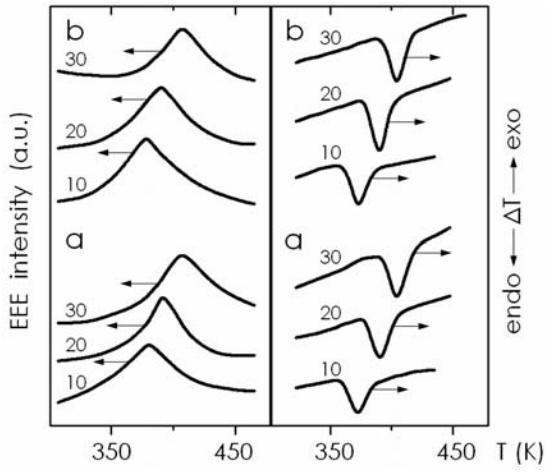

Fig. 1. Temperature dependencies of the DTA signal and exoelectron emission intensity from non-irradiated (*a*) and γ-irradiated (*b*) chalcogenide glasses As_xSe_{100-x} determined at a heating rate of 5 K/min. Parameter – As-content (x) in the sample

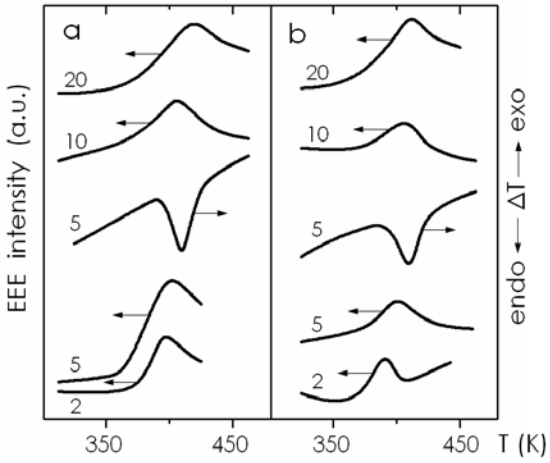

Fig. 2. Temperature dependencies of the DTA signal and the intensity of EEE from non-irradiated (*a*) and γ-irradiated (*b*) $As_{30}Se_{70}$ samples. Parameter – heating rate in K/min

Figure 2 represents the temperature dependencies of the DTA signal and of the intensity of photostimulated exoelectron emission (EEE) from non- irradiated (*a*) and γ-irradiated (*b*) chalcogenide glass $As_{30}Se_{70}$, measured at different heating rates. The parameter of the curves shown in fig. 2 is the heating rate in K/min. The temperature of the anomalies occurring on the DTA and EEE curves presented in fig. 2 systematically shifts toward higher values with increasing the heating rate. This confirms that the process responsible for the occurrence of these anomalies (retrification) is an thermally activated process.

Measurements of the temperature dependencies of EEE intensity at four different heating rates (2, 5, 10 and 20 K/min), and the DTA curves at five heating rates (1, 2, 5, 10 and 20 K/min) enabled the determination of the activation energy for the retrification

process at the surface and in the volume of the samples, responsible for the occurrence of the maxima on the EEE and DTA curves, correspondingly. Activation energy was determined using the well-known Ozawa relation [12]:

$$\ln v = A - \frac{E}{kT}$$

where v is the heating rate, A – constant, E – activation energy, k – Boltzmann's constant and T – transformation temperature.

The retrification temperature T has been determined from the position of the maximum on the EEE curves [13], and as the deflection point (from the base line) on the DTA curves [14].

Activation energy of the retrification process is a parameter characterizing well the thermal stability of amorphous materials. The values of the activation energy for the retrification process in the surface layer and in the volume of non-irradiated and γ-irradiated chalcogenide glass As_xSe_{100-x}, determined in the present study on the basis of systematic EEE and DTA investigations by the Ozawa method, are collected in table 1. For both the non-irradiated and γ-irradiated As_xSe_{100-x} samples the activation energy for the surface retrification is smaller than that for volume retrification. Thermal stability of the γ-irradiated samples is greater than that of the non-irradiated material (activation energy for retrification process in irradiated samples is greater than that for non-irradiated material).

Table 1

Activation energies for the volume and surface retrification of investigated As_xSe_{100-x} chalcogenide glasses as determined from the DTA and EEE measurements, respectively

As content, x, type of sample	Activation energy in eV	
	Surface retrification	Volume retrification
10 – a	0,75	1,91
10 – b	0,83	1,99
20 – a	1,10	1,61
20 – b	1,21	1,74
30 – a	1,28	1,62
30 – b	1,40	–

From the results of the present study it follows out that:
- retrification processes in the surface layer occurs with an activation energy smaller than that in the volume,
- γ-irradiation causes an increase in the value of the activation energy for retrification process in both the surface layer and in the volume, thus enhancing the thermal stability of chalcogenide glasses As_xSe_{100-x} (see also [5]),
- the combination of the EEE and DTA methods would be very useful and efficient in investigations of the crystallization kinetics and thermal stability of chalcogenide glasses.

Further studies are in progress.

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ТЕРМІЧНА СТАБІЛЬНІСТЬ ТА КІНЕТИКА СТРУКТУРНИХ ПЕРЕТВОРЕНЬ СКЛОПОДІБНИХ ХАЛЬКОГЕНІДНИХ НАПІВПРОВІДНИКІВ СИСТЕМИ As_xSe_{100-x}

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Досліджено кінетику фазових переходів в γ-опромінених і неопромінених халькогенідних стеклах As_xSe_{100-x} (x = 10, 20 і 30) методом диференціального термічного аналізу та технікою ексоелектронної емісії. Енергії активації досліджених матеріалів визначались методом Озава. З'ясовано, що енергія активації у поверхневому шарі менша, ніж в об'ємі. Показано, що γ-опромінення поліпшує термостабільності досліджуваних матеріалів.

Ключові слова: халькогенідні стекла, ДТА, екзоелектронна емісія, енергія активації, γ-опромінення.

ТЕРМИЧЕСКАЯ СТАБИЛЬНОСТЬ И КИНЕТИКА СТРУКТУРНЫХ ПРЕВРАЩЕНИЙ СТЕКЛООБРАЗНЫХ ХАЛЬКОГЕНИДНЫХ ПОЛУПРОВОДНИКОВ СИСТЕМЫ As_xSe_{100-x}

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Исследована кинетика фазовых переходов в γ-облученных и необлученных халькогенидных стеклах As_xSe_{100-x} (x = 10, 20 и 30) методом дифференциального термического анализа и техники экзоэлектронной эмиссии. Энергии активации исследованных материалов определялись методом Озава. Установлено, что энергия активации в поверхностном слое меньше, чем в объеме. Показано, что γ-облучение улучшает термостабильность исследуемых материалов.

Ключевые слова: халькогенидные стекла, ДТА, экзоэлектронная эмиссия, энергия активации, γ-облучение.

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