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KINETICS OF PHASE TRANSITIONS IN VITREOUS CHALCOGENIDE SEMICONDUCTORS As_xSe_{100-x} AS STUDIED BY DIFFERENTIAL THERMAL ANALYSIS (DTA) AND EXOELECTRON EMISSION (EEE) METHODS

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Temperature dependencies of the DTA signal and intensity of EEE from γ-irradiated and non-irradiated chalcogenide glasses As_xSe_{100-x} (x = 0, 10, 20, 30, 40 and 50) have been investigated. 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 retrification in the volume. Gamma-irradiation improves the thermal stability of investigated materials.

Key words: chalcogenide glasses, DTA, exoelectron emission, activation energy, retrification, γ – irradiated.

Chalcogenide glasses, 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 [3–5]. The effect of irradiation is an additional factor complicating the control of production of materials with desired (prognozed) properties.

Amorphous materials tend to crystallize (and to loose their unique properties) 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 resulting from the fact, that the parameters characterizing 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].

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 = 0, 10, 20, 30. 40 and 50) as well as the effect of γ-irradiation on these processes and their parameters.

Measurements of the temperature dependencies of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [9]. An open point counter with saturated ethanol quenching vapor was used for detecting the exoelectrons. The sample temperature, controlled using an Pt-PtRh 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. All the EEE measurements were performed in an air atmosphere under ambient pressure.

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

The vitreous samples of As_xSe_{100-x} (x = 0, 10, 20, 30, 40 and 50) 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 the most 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 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).

Temperature dependencies of the intensity of photostimulated exoelectron emission (EEE) and of the differential thermal analysis signal (DTA), for investigated chalcogenide glasses, all measured at the same heating rate of 2 K/min. are shown in Fig. 1. The parameter of the curves presented in this figure is the arsenic content (x) in the sample.

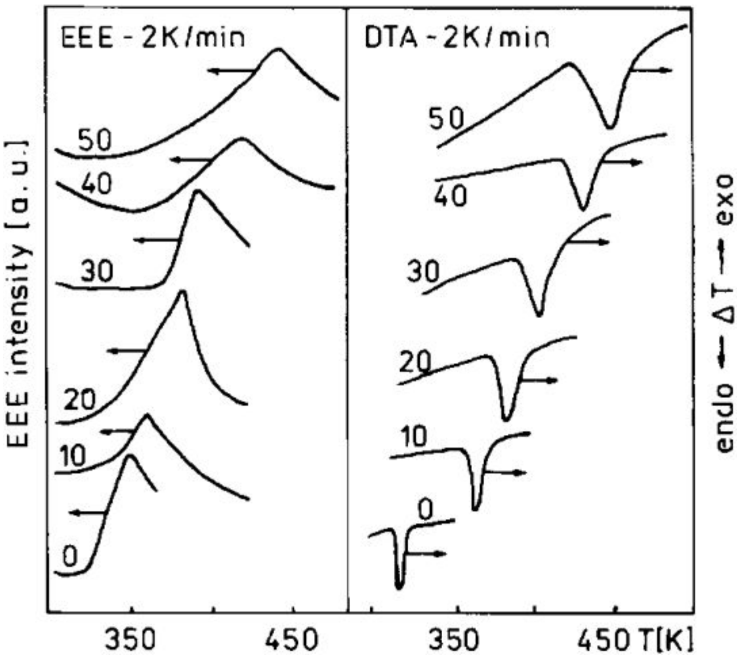

Fig. 1. Temperature dependencies of the DTA signal and exoelectron emission intensity for chalcogenide glasses As_xSe_{100-x} determined at a heating rate of 2 K/min. Parameter – As–content (x) in the sample

The temperature dependencies of the intensity presented in Fig. 1 display a maximum coinciding with the endothermal effect occurring on the DTA curves. The temperature of these anomalies occurring on both the EEE and DTA curves systematically increase with the increase 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. 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 $As_{20}Se_{80}$, 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

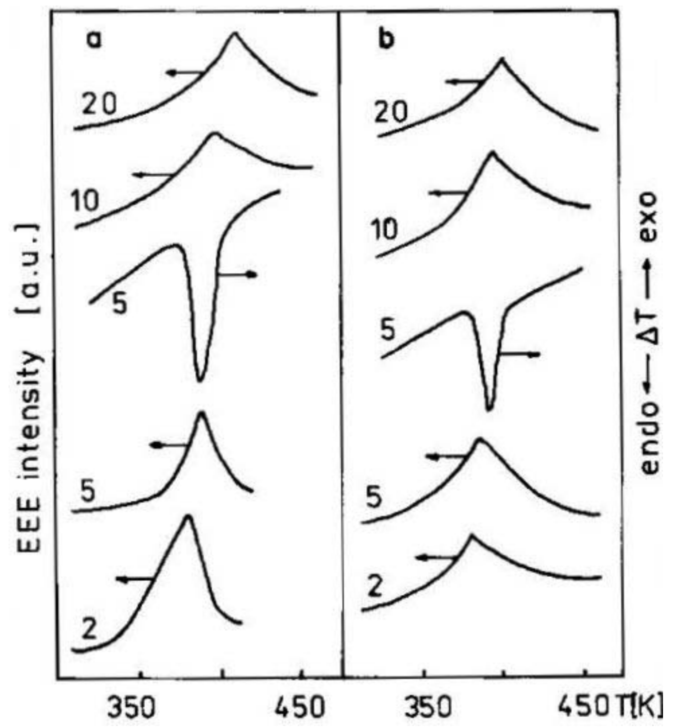

Fig. 2. Temperature dependencies of the DTA signal and the intensity of EEE from non-irradiated (a) and γ-irradiated (b) $As_{20}Se_{80}$ samples. Parameter – heating rate in K/min

DTA and EEE curves presented in Fig. 2 systematically shift 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, and the DTA curves at five heating rates, enabled the determination of the activation energy for the retrification process on 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 [10]:

$$\ln V = A - E/kT$$

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

The dependencies of the transformation (retrification) temperatures T, determined from the temperature dependencies of the EEE intensity and DTA signal, on the heating rate V, represented in the Ozawa coordinates $\ln V = f(1/T)$ (so called Ozawa plots) for non-irradiated and γ-irradiated $As_{20}Se_{80}$ samples are shown on Fig. 3. The retrification temperature T has been determined from the position of the maximum on the EEE curves [11], and as the deflection point (from the base line) on the DTA curves [12].

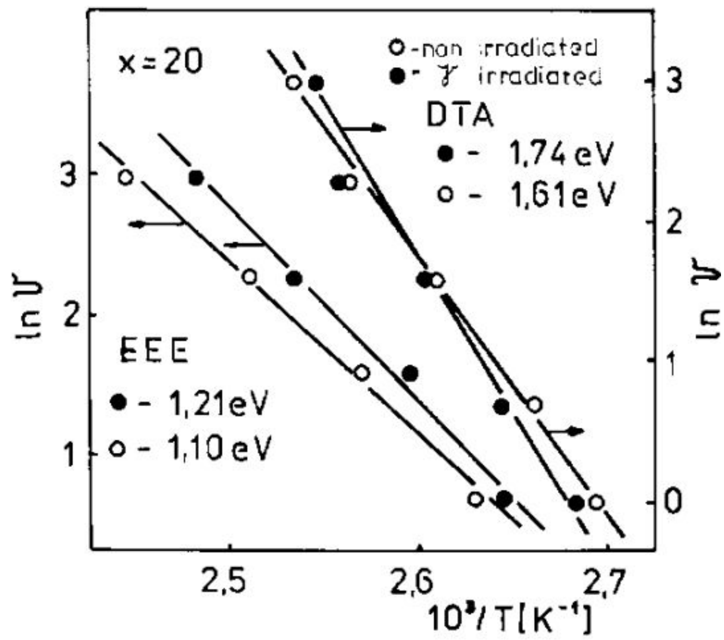

Fig. 3. Ozawa's plots for the surface (EEE) and volume (DTA) retrification process for non-irradiated and γ-irradiated $As_{20}Se_{80}$ samples

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 $As_{20}Se_{80}$, determined in the present study on the basis of systematic EEE and DTA investigations by the Ozawa method, are given on Fig. 3. For both the non-irradiated and γ-irradiated $As_{20}Se_{80}$ 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).

From the results of the present study it follows out that:

- retrification temperature of the As_xSe_{100-x} ($x \leq 50$) glasses increases with increasing arsenic content (x),
- retrification processes in the surface layer occur with a smaller activation energy than 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.

1. *Saiter J.M.* Physical ageing in chalcogenide glass// J. Optoelect. Adv. Mat. 2001. Vol. 3. P. 685–694.
2. *Ohta T., Birukawa M., Yamada N., Hirao K.* Optical phase change and magneto-optical recording// J. Magn. and Magn. Mater. 2002. Vol. 242–245. P. 108–115.
3. *Galemczuk R., Bonjour E.* Gamma-ray induced relaxation in selenium glass// J. Non-Cryst. Solids. 1981. Vol. 43. P. 427–432.
4. *Golovchak R., Górecki Cz., Kozdraś A., Shpotyuk O.* Physical ageing effects in vitreous arsenic selenides// Sol. State Commun. 2006. Vol. 137. P. 67–69.
5. *Golovchak R., Shpotyuk O., Shpotyuk M., Górecki Cz., Kozdraś A.* Ageing effects in $As_{10}Se_{90}$ chalcogenide glasses induced by γ-irradiation// Ukr. J. Phys. 2005. Vol. 50. P. 690–693.
6. *Wagner T., Kasap S.O., Petkow K.* Temperature-modulated differential scanning calorimetry studies of the structure of bulk and thin film $Ge_xAs_yS_{60}$ chalcogenide glasses// J. Mat. Sci. 1997. Vol. 32. P. 5889–5893.
7. *Górecki Cz., Górecki T.,Michno Z.* Thermal stability of the $Fe_{40-x}Ni_{40}Cr_xB_{20}$ metallic glasses as studied by the EEE and DTA methods// Acta Phys. Polon. 1987. Vol. A72. P. 157–160, and Thermal stability of the $Ni_{78}Si_xB_{22-x}$ metallic glasses as studied by the EEE and DTA methods// Acta Phys. Polon. 1987. Vol. A72. P. 161–163.
8. *Górecki Cz., Górecki T., Golovchak R., Żurawska A., Wacke S.* Kinetics of phase transitions in semiconducting amorphous chalcogenides As_xSe_{100-x} as studied by differential thermal analysis and exoelectron emission techniques// Visnyk Lviv. Univ. 2005. Vol. 38. P. 399–403.
9. *Górecki Cz., Górecki T., Szymura S.* Surface and volume crystallization of metallic glass $(Ni_{50}Zr_{50})_{99.9}P_{0.1}$ as investigated by exoelectron emission (EEE) and differential thermal analysis (DTA)// Modern Phys. Lett. 2002. Vol. 16. P. 87–92.
10. *Ozawa T.* Kinetics of non-isothermal crystallization of amorphous materials// J. Thermal Anal. 1970. Vol. 2. P. 301–312.
11. *Sujak B., Górecki T.* Egzoemisja elektronów podczas przemian fazowych i reakcji w ciałach stałych// Wiadomości Chemiczne, 1973. Vol. 37. P. 361–384.
12. *Schultze D.* Termiczna Analiza Różnicowa: PWN, 1974.

МЕТОДИ ДИФЕРЕНЦІАЛЬНОГО ТЕРМІЧНОГО АНАЛІЗУ (ДТА) ТА ЕКЗОЕЛЕКТРОННОЇ ЕМІСІЇ (ЕЕЕ) В ЗАСТОСУВАННІ ДО КІНЕТИКИ ФАЗОВИХ ПЕРЕХОДІВ У СКЛОПОДІБНИХ ХАЛЬКОГЕНІДНИХ НАПІВПРОВІДНИКАХ СИСТЕМИ As_xSe_{100-x}

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Досліджено температурну залежність сигналу ДТА та інтенсивності ЕЕЕ для γ-опромінених та неопромінених халькогенідних стекол системи As_xSe_{100-x} (x = 0, 10, 20, 30, 40 і 50). Енергії активації процесу переходу скла у термодинамічно-рівноважний стан переохолодженої рідини визначено методом Озави. З’ясовано, що ці енергії для поверхневих шарів є меншими, ніж для об’єму. Гамма-опромінення покращує термічну стабільність досліджуваних стекол.

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

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