AGEING EFFECTS IN $As_{10}Se_{90}$ CHALCOGENIDE GLASSES INDUCED BY γ-IRRADIATION

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The peculiarities of γ-induced (Co^{60}source, 1.85 MGy absorbed dose) ageing phenomena in $As_{10}Se_{90}$ chalcogenide glasses are investigated for the first time. The analogy between the observed radiation-induced ageing and the thermally induced one in vitreous selenium is emphasized. Like to thermal treatment, γ-irradiation leads to an increase in the glass transition temperature and the relaxation rate towards a thermodynamic equilibrium of supercooled liquid, the value of this increase being greater in the case of radiation influence.

1. Introduction

Chalcogenide glasses (ChG), obtained as alloys of chemical elements from the IV and V groups of the Periodic Table with chalcogens (S, Se and Te, but not O), are perspective materials for optoelectronics [1—4], their semiconducting properties being firstly discovered by B.T. Kolomiets and N.O. Goryunova in the 1960s [1]. However, the wide application of ChG is limited by their structural metastability which is a common feature of all disordered materials. The reason for metastability is connected with a technological route of ChG preparation, the quenching of a melt. This synthesis procedure causes some peculiarities of liquid to be remained in the vitreous state [5, 6]. As a result, the thermoinduced ageing is characteristic of ChG. It means that the long-term isothermal annealing leads to the approaching of the ChG enthalpy to a thermodynamic equilibrium of supercooled liquid [7].

It is obvious that the ageing can be stimulated not only by a thermal influence. Using the differential scanning calorimetry (DSC) technique, it was shown that γ-quanta from ^{60}Co sources produce a similar effect in vitreous Se and lead to an increase of the glass transition temperature T_g and the relaxation rate towards thermodynamic equilibrium states of supercooled liquid [8]. So, the entropy of γ-irradiated Se samples was lower than that of non-irradiated ones which were isochronically annealed at the same temperature without radiation.

Unfortunately, the above experiment has a number of inaccuracies. The authors did not separate the influence of annealing temperature and different doses of γ-irradiation. The role of uncontrolled thermal heating, which accompanied γ-irradiation, remains unclear. Apart from this, vitreous Se has a too low T_g value close to room temperature (~300 K) and a high crystallization ability [5]. But, it is well known that the lower the temperature of γ-irradiation (in respect to T_g), the greater the induced effect owing to the lesser probability of thermally stimulated self-restoration processes during the radiation treatment [9]. Thus, vitreous Se is not a convenient object for the observation of γ-induced effects due to self-annealing processes near T_g.

The problem of ChG radiation-induced ageing didn't brought up at all during more than last 20 years. Today, this caused many additional complications, especially in the development of controlled technological routes for the synthesis of vitreous media with predicted functional properties.

In this paper, ChG of the $As_{10}Se_{90}$ composition are investigated using the DSC method. On the one hand, this glass possesses a structure close to that of vitreous Se. On the other hand, the $As_{10}Se_{90}$ ChG has higher T_g (~360 K [5]), which prevents the quick self-restoration of γ-induced changes during a γ-treatment and a sample storage under natural conditions.

2. Objects and Methods of Investigation

The investigated v-$As_{10}Se_{90}$ samples were prepared by the standard melt-quenching method, using a highpurity (99.999 %) mixture of As and Se precursors. The obtained samples were divided into 2 parts, the first one being stored at room temperature, and another one being γ-irradiated under natural conditions. The absorbed radiation dose of 1.85 MGy (Co^{60} source) lies in the range of the maximal radiation sensitivity for ChG [9].

The DSC measurements were performed on a pre-calibrated NETZSCH 404/4 microcalorimeter (Germany). The non-irradiated and γ-irradiated samples were measured at different heating rates q ranging from 1 to 20 K/min during one week after γ-irradiation. All investigated samples were stored under identical conditions before measurements. The glass transition temperature T_g was estimated at the cross-point of tangents at the beginning of the glass—supercooled liquid phase transition (the so-called "*onset*" T_g value) [5]. The maximum error of the T_g determination did not exceed ±0.3 K (including the equipment accuracy).

3. Results and Discussion

The DSC curves of non-irradiated and γ-irradiated $As_{10}Se_{90}$ ChG, obtained at different heating rates q are shown in Fig. 1, the numerical parameters of the corresponding relaxation processes being presented in Table.

Apparently, the increase of specific heat capacity ΔC_p during the transition of ChG into the supercooled liquid state is well-expressed on the DSC curves as an endothermic shift of the basic line. The effect of radiation influence consists in an increase of the glass transition temperature T_g, area A, and intensity I of the endothermic peak in the region of the glass—supercooled liquid phase transition. As far as the nature of this peak is connected with relaxation transformations in a glass-like network [5,7], the γ-induced changes in parameters of the structural relaxation for $As_{10}Se_{90}$ ChG are obvious.

It is interesting that, despite a regular increase in the glass transition temperature T_g with the heating rate q for both non-irradiated and γ-irradiated $As_{10}Se_{90}$ samples, the value of radiation-induced ΔT_g changes remains at a level of ~3.0 K with the average deviation ±0.3 K (Table) which is comparable with the T_g determination accuracy. At the same time, the γ-stimulated changes of quantitative descriptive parameters for the endothermic peak in the region of the glass—supercooled liquid phase transition exhibit a

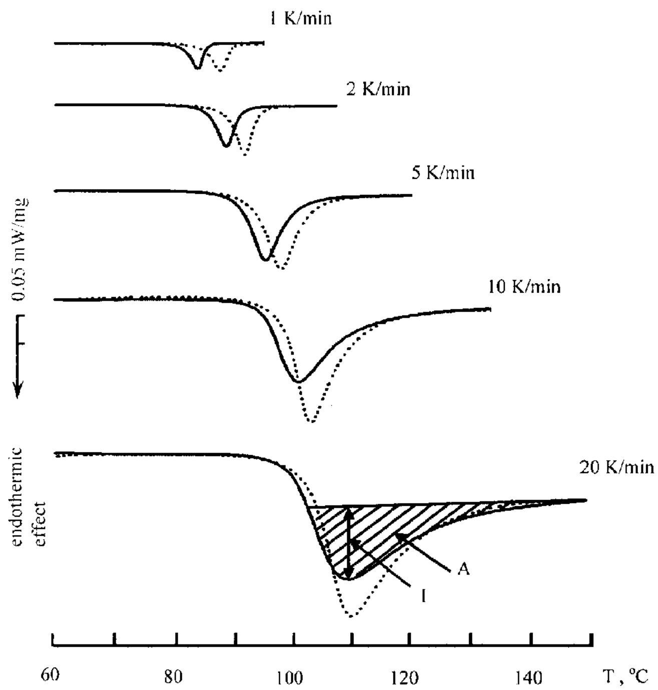

Fig. 1. DSC traces of non-irradiated (solid curve) and γ-irradiated (dotted curve) $As_{10}Se_{90}$ ChG, obtained at the heating rates q (up to down) 1, 2, 5, 10, and 20 K/min (in the last case, the area A and intensity I of the endothermic peak in the region of the glass—supercooled liquid phase transition are indicated)

rough dependence on q. The gradual increase of ΔA and $\Delta I/I_0$ values with q is a typical feature (see Table).

Using the Ozawa method [10], it is possible to determine the activation energy ΔE_a of a viscous flow for ChG. For γ-irradiated $As_{10}Se_{90}$ samples, ΔE_a equals 1.99 eV/at., that is by ~0.08 eV/at. greater than that for non-irradiated ChG (1.91 eV/at.). It should be noted that the above-calculated ΔE_a values are comparable with the dissociation energies of Se-Se (~1.9 eV) and As-Se (~1.8 eV) covalent bonds [11].

The analysis of the observed γ-induced relaxation effect in the investigated ChG shows its analogy with

Parameters of structural relaxation in $As_{10}Se_{90}$ ChG before and after γ-irradiation

q, K/min	T_g, K			A, (J·K)/(g·s)			$\Delta I/I_0$, %
	T_g^0 before γ	T_g^γ after γ	ΔT_g K	A_0 before γ	A^γ after γ	ΔA	
1	355.0	358.3	3.3	0.12	0.16	0.04	~ 10
2	359.1	362.2	3.1	0.27	0.33	0.06	~ 25
5	364.3	366.7	2.4	0.71	0.86	0.15	~ 20
10	368.2	371.5	3.3	1.40	1.82	0.42	~ 60
20	372.9	375.8	2.9	1.62	2.29	0.67	~ 65

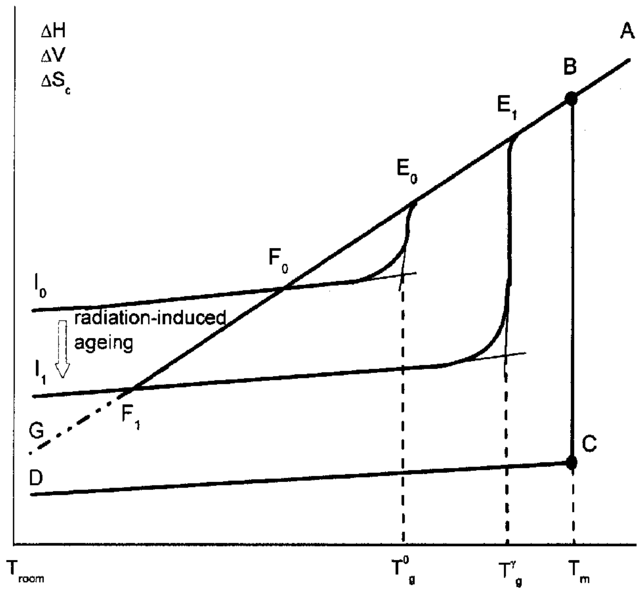

Fig. 2. Enthalpic diagram of γ-induced ageing in Se-based ChG

the thermoinduced physical ageing in vitreous Se [7,8]. However, the quantitative values of the descriptive parameters for the γ-induced ageing phenomenon are rather different from those proper to the isochronal thermal ageing of non-irradiated samples. From the obtained experimental data, it is clear that γ-irradiation of vitreous $As_{10}Se_{90}$ strengthens the normal thermoinduced ageing effect.

The enthalpy diagram in Fig. 2 showing the transition from a metastable low-temperature solid state of the vitreous material to a high-temperature state of melt represents the specificity of the considered processes for selenium-based ChG. Let's assume that, in the case of non-irradiated ChG, this transition is given by curve $I_0F_0E_0B$. An increase of the endothermic peak area A on the DSC traces for γ-irradiated $As_{10}Se_{90}$ samples together with a high-temperature shift of T_g (Fig. 1) says that the metastable vitreous state of the system after irradiation becomes closer to the extrapolated thermodynamic equilibrium states of supercooled liquid (E_0G in the enthalpy diagram, Fig. 2). Because the difference between the endothermic peak intensities and the areas for γ-irradiated and non-irradiated ChG is connected with changes in the rate of regaining the thermodynamic equilibrium [8], the increase in the structural relaxation rate through the region of the glass—supercooled liquid phase transition (like in the case of prolonged isothermal ChG annealing [7]) can be attributed to the effect of γ-irradiation.

To explain the nature of the observed radiation-induced ageing effect in ChG, γ-induced microstructural changes should be considered. It is well known that γ-irradiation leads to the intensive processes of covalent bond destruction due to the electron excitation decay [12]. Depending on the ChG composition, the final products of these processes can be stabilized in the form of the so-called coordination defect pairs (oppositely charged over- and under-coordinated atoms), when the average connectivity of a glass-forming matrix restores through new covalent bonds [9, 13, 14] or in the form of radiation-modified normally coordinated structural fragments, when the broken bond recovers or a created coordination defect pair annihilates by the backward bond switching.

So, two types of independent processes are possible in ChG as a result of γ-irradiation [9, 13—15]. The first one is connected with the covalent chemical bond switching and the simultaneous formation of pairs of oppositely charged coordination defects, slight structural changes occurring at the medium range ordering level (rotation of some structural fragments, displacements of atom and their groups). The second process involves the reorientation of atoms and more extended structural fragments of the glassy network without any changes in the local atomic coordination or the type of covalent bonds. In the first case, the average energetic connectivity of the ChG matrix decreases, as a rule, owing to the formation of "unfavorable" covalent chemical bonds under low-temperature conditions of γ-treatment. By other words, γ-irradiation disturbs the initial balance of covalent bonds in ChG and leads to the appearance of weaker (first of all, homopolar) chemical bonds instead of stronger ones (heteropolar, in part) [9, 15]. The difference in the configuration coordinates of the corresponding metastable states, which depends on the molar volume of ChG, prevents the backward annihilation of created coordination defects. In the second case, the ChG structure partially orders after γ-irradiation [9] and approaches the extrapolated thermodynamic equilibrium states of supercooled liquid (Fig. 2), keeping the energetic connectivity of the ChG matrix unchangeable.

The relationship between these concurrent processes depends on the chemical composition of ChG. If the radiation-induced coordination defect formation processes prevail, as in the case of sulfide-based ChG [13—15] where the energetic barrier of covalent bond switching is high, the ChG system shifts away from the extrapolated thermodynamic equilibrium states of supercooled liquid. Otherwise, if the defect-free

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processes overrule, the glass approaches the extrapolated thermodynamic equilibrium states of supercooled liquid [8], as it is characteristic of the relaxation of a "frozen" disorder during thermoinduced ageing [7]. We believe this kind of relaxation processes is proper to the radiation-induced ageing effect in selenium-based ChG and $As_{10}Se_{90}$, in part.

4. Conclusions

It is shown that the γ-induced ageing effect in $As_{10}Se_{90}$ ChG is revealed through a $\sim$3 K increase in their glass transition temperature, $\sim$0.08 eV/at. increase in the activation energy of a viscous flow, as well as a magnification of the area and the intensity of the endothermic peak in the region of the glass—supercooled liquid phase transition and, consequently, an increase in the relaxation rate towards a thermodynamic equilibrium of supercooled liquid. The qualitative analogy between the radiation-induced ageing of $As_{10}Se_{90}$ ChG and the thermoinduced ageing of vitreous arsenic selenides is emphasized.

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ЕФЕКТИ СТАРІННЯ В ХАЛЬКОГЕНІДНИХ СТЕКЛАХ $As_{10}Se_{90}$, ВИКЛИКАНІ γ-ОПРОМІНЕННЯМ

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Р е з ю м е

Досліджено особливості γ-індукованого (джерело Co^{60}, поглинута доза 1,85 МГр) старіння халькогенідних стекол (ХС) $As_{10}Se_{90}$. Показана подібність даних процесів до термоіндукованого старіння склоподібного селену. Встановлено, що, як і у випадку ізотермічного відпалу, внаслідок γ-опромінення зростає температура початку фазового переходу скло—переохолоджена рідина та збільшується швидкість структурної релаксації системи до термодинамічно рівноважних станів переохолодженої рідини, причому за величиною радіаційно-індуковані зміни є більшими в порівнянні з термоіндукованими.