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INFLUENCE OF γ-IRRADIATION ON PHYSICAL AGEING IN As-Se GLASSES

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Effect of external influences on physical ageing processes in As-Se chalcogenide glasses is studied at the example of Co^{60} γ-irradiation. The increase in glass transition temperature and endothermic peak area near glass transition region for Se-enriched glasses is shown by differential scanning calorimetry method as a result of radiation treatment. The observed changes are associated with additional γ-activated structural relaxation of glass network towards thermodynamic equilibrium of supercooled liquid.

Key words: chalcogenide glasses, physical ageing, γ-irradiation, differential scanning calorimetry.

Physical ageing effects in chalcogenide glasses (ChG) [1, 2], associated with slow structural relaxation towards thermodynamic equilibrium of supercooled liquid, sufficiently restrict their practical application because of uncontrolled drift in the exploitation characteristics of ChG-based devices. In other words, ChG kept far below glass transition temperature T_g lose their excess of configurational entropy, enthalpy or free volume (gained at the stage of synthesis) to reach a more favorable thermodynamic state. But the same changes could appear not only during isothermal storage, but under influence of additional external causes such as foto- or γ-irradiation too [3, 4].

To study the influence of external factors on physical ageing in As-Se ChG the γ-irradiation was chosen as a model type of high-energy ionizing irradiation. As a result, the changes produced by γ-irradiation are uniform through the whole bulk of ChG, being large enough to be recorded experimentally by conventional differential scanning calorimetry (DSC) method [4].

The investigated samples of As_xSe_{100-x} ChG (x = 0, 10, 20, 30, 40, 45, 50, 53, 55 and 60) were obtained by conventional melt quenching (regime of switched-off furnace) in the evacuated quartz ampoules from a mixture of high purity (99,999 %) precursors. The γ-irradiation procedure was carried out in the closed cylindrical cavity of concentrically established Co^{60} sources (mean energy – 1,25 MeV) with a few Gy/s power. The total duration of γ-irradiation was nearly 2 months, the accumulated dose being as high as 2,4 MGy. Differential scanning calorimetry (DSC) measurements were

performed on NETZSCH 404/4 microcalorimeter. The DSC traces were recorded in the ambient atmosphere with q = 5 °C/min heating rate.

The investigated ChG samples were measured just after preparation, during next 4 months before γ-irradiation and just after γ-irradiation. Before the measurements, all samples were stored in dark under normal conditions. The 4-months time interval before γ-irradiation allowed to exclude the influence of fast relaxation processes (or conventional natural ageing effects) in all investigated ChG samples despite their composition [1, 2, 5]. In such way, the short-term natural physical ageing effects were separated from γ-induced ones.

As it can be seen from the obtained experimental results (Table 1), the T_g of as-prepared ChG and its compositional dependence fully correlates with known from the literature data [6]. The A values determined from DSC traces just after preparation are small for all ChG not exceeding ~ 1 J/g. They can be considered as a level of pure structural relaxation effects, occurred in As-Se ChG through a glass-to-supercooled liquid phase transition at given q [6, 7].

The followed natural storage affected A and T_g parameters for the investigated As_xSe_{100-x} ChG with $x < 30$. The drastic effect of increase in endothermic peak area A and T_g values (see Table 1) was observed, reaching the saturation during first 1-4 months (depending on x) of storage. The significant natural ageing effect is obvious for Se, $As_{10}Se_{90}$ and $As_{20}Se_{80}$ ChG, but only slight changes (not exceeding experimental error) are recorded for all the rest ChG with $x \geq 30$. The analogous compositional behaviour of short-term natural physical ageing was observed in As-Se ChG using temperature modulated DSC technique [4]. On the basis of these results, a so-called reversibility window $29 \leq x \leq 37$ (the range of ChG compositions where no ageing effects occur) was detected in these materials [1, 8]. The glasses with $x > 37$ were supposed to be sensitive to ageing, but the conditions had to be harsher than the natural.

Table 1

Glass transition parameters determined from DSC traces of as-prepared, 6-months aged and γ-irradiated As-Se ChG

ChG composition	T_g-onset, °C			Peak area A, J/g		
	as-prepared	aged without irradiation	aged with γ-irradiation	as-prepared	aged without irradiation	aged with γ-irradiation
Se	37,3	49,0	51,4	0,3	5,1	6,0
$As_{10}Se_{90}$	69,7	88,1	96,3	0,7	8,5	13,3
$As_{20}Se_{80}$	94,0	96,7	107,0	0,6	3,8	7,6
$As_{30}Se_{70}$	115,2	115,3	115,7	1,2	1,4	1,5
$As_{40}Se_{60}$	178,9	179,8	180,1	0,9	1,6	1,4
$As_{45}Se_{55}$	179,1	179,9	179,7	0,9	0,5	0,3
$As_{50}Se_{50}$	162,1	164,9	164,2	0,3	0,2	0,1
$As_{53}Se_{47}$	147,9	148,3	148,5	0,7	0,4	0,6
$As_{55}Se_{45}$	134,6	135,9	136,9	~0	~0	~0
$As_{60}Se_{40}$	175,5	176,3	175,9	0,8	0,7	0,6

Two-months γ-irradiation led to further increase in T_g and endothermic peak area A for As_xSe_{100-x} ChG with $x < 30$ too. Owing to the analogous behavior in DSC data (like in the case of natural physical ageing), it can be concluded that γ-irradiation modifies

covalent-bonded glass networks of Se, $As_{10}Se_{90}$ and $As_{20}Se_{80}$ ChG towards thermodynamically equilibrium extrapolated states of supercooled liquid. The same conclusion was put forward previously for γ-irradiated vitreous Se, showing a similar behaviour in DSC traces [9]. There were no detectable γ-induced changes (within accuracy error) in the studied As_xSe_{100-x} ChG with $x \geq 30$ (see Table 1) even for glasses over the upper compositional limit of the reversibility window ($x = 37$ [1]).

So, it is shown that high-energy γ-irradiation stimulates additional physical ageing in As_xSe_{100-x} ChG with $x < 30$ over the natural one. This effect is expressed on DSC traces as increase in glass transition temperature and endothermic peak area in the vicinity of glass transition region. Using the analogy with natural physical ageing, it is assumed that structural network of γ-irradiated ChG relaxes in a new thermodynamic state, which is closer to equilibrium of supercooled liquid.

1. *Georgiev D.G., Boolchand P., Micoulaut M.* Rigidity transitions and molecular structure of As_xSe_{1-x} glasses // Physical Review B. Vol. 62. № 14. P. R9228–R9231.
2. *Tonchev D., Kasap S.O.* Effect of aging on glass transformation measurements by temperature modulated DSC // Materials Science and Engineering. Sec. A. 2002. Vol. 328. P. 62–66.
3. *Lucas P., King E.A., Doraiswamy A., Jivaganont P.* Competitive photostructural effects in Ge-Se glass // Physical Review B. 2005. Vol. 71. P. 104207-1-104207–6.
4. *Golovchak R., Shpotyuk O., Shpotyuk M., Gorecki Cz.* et al. Ageing effects in $As_{10}Se_{90}$ chalcogenide glasses induced by γ-irradiation // Ukr. J. Phys. 2005. Vol. 50. N 7. P. 690–693.
5. *Hach C.T., Cerqua-Richardson K., Varner J.R.* et al. Density and microhardness of As-Se glass fibers // J. Non-Cryst. Solids. 1997. Vol. 209. P. 159–165.
6. *Feltz A.* Amorphous and vitreous inorganic solids. Moscow: Mir, 1986. P. 558.
7. *DeBolt M.A., Easteal A.J., Macedo P.B., Moynihan C.T.* Analysis of structural relaxation in glass using rate heating data // J. American Ceram. Society. 1976. Vol. 59. № 1-2. P. 16–21.
8. *Chakrawarty S., Georgiev D.G., Boolchand P., Micoulaut M. J.* Ageing, fragility and the reversibility window in bulk alloy glasses // J. Phys.: Condens. Matter. 2005. Vol. 17. P. L1–L7.
9. *Calemczuk R., Bonjour E. J.* Gamma-ray induced relaxation in selenium glass // J. Non-Cryst. Solids. 1981. Vol. 43. P. 427–432.

ВПЛИВ γ-ВИПРОМІНЮВАННЯ НА ФІЗИЧНЕ СТАРІННЯ В As-Se СТЕКЛАХ

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На прикладі γ-випромінювання від джерела Co^{60} досліджено ефект зовнішнього впливу на процес фізичного старіння халькогенідних стекол системи As-Se. Як результат радіаційної обробки методом диференціальної скануючої калориметрії було зафіксовано підвищення температури фазового переходу та площі ендотермічного піку в області фазового переходу скло–переохолоджена рідина для Se-збагачених стекол. Ці зміни пов’язують з додатковою γ-активованою релаксацією склоподібної матриці до більш термодинамічно рівноважного стану переохолодженої рідини.

Ключові слова: халькогенідні стекла, фізичне старіння, γ-випромінювання, диференціальна скануюча калориметрія.

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