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Short Communication

High-energy γ-irradiation effect on physical ageing in Ge–Se glasses

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ABSTRACT

Effect of Co^{60} γ-irradiation on physical ageing in binary Ge_xSe_{100-x} glasses ($5 \leqslant x \leqslant 27$) is studied using conventional differential scanning calorimetry method. It is shown, that high-energy irradiation leads to additional increase in the glass transition temperature and endothermic peak area near the glass transition region over the one induced by isochronal storage of these glasses at normal conditions. This γ-induced physical ageing is shown to be well-pronounced in Se-rich glasses ($x < 20$), while only negligible changes are recorded for glasses of $20 \leqslant x \leqslant 27$ compositions. The effect under consideration is supposed to be associated with γ-activated structural relaxation of the glass network towards thermodynamic equilibrium of supercooled liquid.

1. Introduction

Chalcogenide glasses (ChG) of binary Ge–Se family are known to be promising materials for application in optoelectronics, photonics, biomedicine and IR telecommunication [1–6]. In particular, they can be effectively used as IR optical lenses and fibers [1], bio-sensors [1,2], media for grey-scale photolithography [3], Li-ion transport [4] and nanoionic nonvolatile memory devices [5].

These numerous applications require a detailed knowledge on a glass structure as well as its behavior under the influence of different external factors. Despite of significant number of researches devoted to the influence of photoexposure [6–8], mechanical stresses [9], electromagnetic and thermal fields [10,11], the effects induced by high-energy radiation such as ^{60}Co γ-quanta in these glasses remained out of the scope. This kind of irradiation, owing to a high penetration ability and low cross-section of absorption of γ-quanta, provides a powerful tool for examination of pure athermal structural transformations inside the whole bulk of the material [12]. Absence of atomic transmutations and surface damages character for corpuscular type of irradiations, such as neutrons, protons or fast electrons, is also an important advantage of γ-irradiation [12,13].

The last-years investigations showed that γ-irradiation was able to modify structural relaxation processes in glass below its glass transition temperature, known also as radiation-induced physical ageing effect [14–16]. Thus, the increased rate of structural relaxation was recorded previously for Se-rich fragile As–Se [14], As–Ge–Se [15] and Sn–Se [16] glasses under the influence of γ-radiation. In contrast to these glasses, the phenomenon of physical ageing in Ge–Se ChG exhibits sometimes an unusual behavior during long-term period of natural storage expressed in a double-peak relaxation through glass-to-supercooled liquid transition [17,18], which structural origin is not quite clear. Since structural relaxation kinetics far below the glass transition temperature is very slow (usually tens of years) [19,20], it is not a trivial task to study the long-term physical ageing in ChG. So, the possibility to accelerate physical ageing in these glasses using γ-radiation treatment seems to be very attractive.

In present paper, we imply ^{60}Co γ-irradiation as effective modification factor for physical ageing in Ge–Se glasses to reveal features of their structural relaxation far below the glass transition interval.

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2. Experimental

The vitreous samples of Ge_xSe_{100-x} (x = 5, 8, 10, 20, 23, 25, 27) compositions were obtained by conventional melt-quenching technique. The mixture of high-purity precursors was melted in the evacuated quartz ampoules at 700 °C for Se-rich samples (x < 10) and at 900 °C for Ge-rich samples during 5 h in a rocking furnace. Then, the ingots were air-quenched from 630–650 °C to obtain glass. The vitreous state was controlled visually by a character conch-like fracture, data of X-ray diffraction and IR microscopy.

Before the experiment had started, all the samples were subjected to a rejuvenation procedure, which included heating of the samples ~50 °C above the onset of their calorimetric glass transition temperatures, equilibrating of the obtained supercooled liquid and further its cooling with the rate q > 5 °C/min to the room temperature. In such a way, it is possible to achieve glassy state, which is close to the initial as-prepared one [17,18]. All the rejuvenated samples were divided into 2 batches. The first batch of samples was stored in hermetic plastic bags in the dark under controlled normal conditions, while the other one was disposed within the γ-irradiation chamber.

The γ-irradiation procedure was carried out at the ambient conditions in a closed cylindrical cavity of concentrically established Co^{60} sources (mean energy – 1.25 MeV) with a few Gy/s power at a temperature not exceeding 28 °C. The total duration of γ-irradiation was 2 months, the accumulated dose being as high as 0.8 MGy. No special efforts were made to exclude the water/air influence during irradiation. In such a manner, the difference between conditions of natural storage and radiation treatment of the investigated samples was minimized.

The samples of two batches were measured simultaneously using NETZSCH 404/3/F microcalorimeter before γ-irradiation (or storage) and just after γ-irradiation (or, consequently, after natural storage of the rejuvenated samples during same period of time). The DSC traces were recorded in the ambient atmosphere with q = 5 °C/min heating rate. Three independent DSC measurements with samples of close masses were performed for each ChG composition to confirm the reproducibility of the results. Glass transition temperature T_g was determined from DSC heating data in cross-point of tangents at the beginning of glass-to-supercooled liquid transition (a so-called "onset" T_g value), using PROTEUS ANALYSIS – NETZSCH PC software. This software was also used for the determination of endothermic peak area A in the vicinity of glass transition. Statistical deviation of T_g for different samples of the same prehistory did not exceed ±0.3 °C (otherwise, the error bar is indicated), while the error for peak area determination was about 2%.

3. Results and discussion

Usually, glass transition in network glasses is expressed by a character endothermic step-like behavior of experimental DSC traces accompanied by endothermic peak in the vicinity of T_g [21,22]. The origin of this peak normally is associated with structural relaxation of glass network through the glass-to-supercooled liquid transition [22,23]. It also includes the component connected with regaining of the entropy lost during natural storage [17,18,24], photo- or radiation influences [6,7,14,15], which was considered as a signature of physical ageing effect caused by these factors. The area A under the endothermic peak was directly proportional to the enthalpy losses: the greater A, the closer to thermodynamic equilibrium state of supercooled liquid was the glass. So, A value can be considered as a control parameter for quantitative description of physical ageing effect induced by the external factors. Besides the changes in the peak area A as a result of physical ageing, the changes in T_g values were also recorded for some fragile ChG [14,15,17,18,24].

Results on the DSC measurements for rejuvenated (as-prepared), non-irradiated and γ-irradiated samples are presented in Fig. 1. Quantitative characteristics of the physical ageing effects, such as A and T_g values, are given in the Table 1, respectively. The T_g values of the rejuvenated ChG and their compositional dependence (Table 1) fully correlate with those, known from the literature data [22,25]. The A values determined from DSC traces just after rejuvenation procedure do not exceed ~0.3 J/g for all investigated glasses, which can be considered as a level of pure structural relaxation effect occurred in these materials through a glass-to-supercooled liquid transition at given q [22,23].

Two months of natural storage changed A and T_g parameters for the investigated Ge_xSe_{100-x} ChG with x < 20. In particular, the increase in the endothermic peak area A and T_g values (see Table 1) was observed for these samples similar to the behavior obtained earlier for Se-rich As–Se glasses [14]. The DSC traces of Ge_5Se_{95}, Ge_8Se_{92}, $Ge_{10}Se_{90}$, $Ge_{12}Se_{88}$, $Ge_{20}Se_{80}$ and $Ge_{23}Se_{77}$ ChG recorded just after rejuvenation and after 2 months of natural storage are shown in Fig. 1 by solid (black) and dotted (blue) curves, respectively. A significant natural physical ageing effect is evident for Ge_5Se_{95}, Ge_8Se_{92} and $Ge_{10}Se_{90}$ ChG, the slight changes are recorded also for $Ge_{12}Se_{88}$ sample, but no physical ageing effect (changes do not exceed the experimental error) is observed for all the rest Ge_xSe_{100-x} compositions with $x \geqslant 20$. Analogous compositional dependences of short-term and long-term natural physical ageing effects were observed in Ge–Se ChG using temperature modulated and conventional DSC techniques [25,26].

The DSC traces of γ-irradiated ChG are shown by dash (red) curves in Fig. 1. Hence, two months of ageing within the γ-radiation field conditions caused a greater increase in T_g and endothermic peak area A values for Se-rich Ge_xSe_{100-x} ChG with x < 20, than the two months of natural storage did. However, no detectable γ-induced changes (within the accuracy error) were recorded in the studied Ge_xSe_{100-x} glasses with $x \geqslant 20$ (see Table 1). At the same time, the changes produced by γ-irradiation in DSC traces of Ge_xSe_{100-x} ChG with x < 20 are similar to those observed after longer period of natural storage comparable with ~years time-scale [26]. Thus, we can speak about acceleration of physical ageing effect by radiation treatment. In other words, γ-irradiation modifies glass networks of Se-rich Ge_xSe_{100-x} ChG towards thermodynamically equilibrium extrapolated states of supercooled liquid. The same conclusion was drawn previously for γ-irradiated vitreous Se [27], As–Se [14], As–Ge–Se [15] and Sn–Se [16] glasses showing a similar behavior in DSC traces after γ-irradiation. So, having all this row of materials we can generalize now that *radiation treatment of Se-rich fragile glasses at normal conditions results in the acceleration of physical ageing effect and related structural relaxation far below glass transition range*. It should be noted here, that in the case of fragile Ge–Se glasses the similar phenomenon was observed also under the influence of sub-bandgap light irradiation [6,7].

Atomistic model of the natural physical ageing effect developed recently at the example of Se-rich As–Se glasses considers physical ageing as a complicated process, which consists of two components called short-term and long-term physical ageing, respectively [26,28,29]. The first one (short-term) is associated with the alignment of Se polymeric chains (can be alternatively understood as transition from *cis*- to *trans*-conformations of Se atoms in chain within a so-called double-well potential) followed by a shrinkage of surrounding network [28]. This is a relatively fast process, which can be activated at room temperatures. The second component, long-term physical ageing, is associated with prolonged overall shrinkage of under-constrained glass network (i.e. the number of constraints per atom n_c is less than 3), which can be accompanied by chemical bonds redistribution [29]. When polymeric Se chains