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Abstract
Glasses of the As–Se system have been used as model objects of the covalent disordered inorganic polymers to investigate the correlation between the cooperative rearranging region (CRR) size determined at the glass transition temperature and the free volume fraction in the glassy state. The CRR size has been determined using temperature modulated differential scanning calorimetry data according to Donth's approach, while the free volume fraction in the investigated materials has been estimated using positron annihilation lifetime spectroscopy data. The obtained results testify that the appearance of open-volume defects greater than 80 Å^3 leads to a significant decrease in the CRR size.

1. Introduction

Relaxation processes in various polymer materials have been extensively studied recently in order to understand their nature and to avoid related phenomena such as physical ageing effects [1–3]. In the vitreous phase, relaxation processes are known to be cooperative [4]: the rearranging movement of one structural unit is only possible if a certain number of neighbouring units is also moved. These movements concern molecular/atomic displacements along a polymeric chain and/or a part of various structural units belonging to neighbouring chains. Adam and Gibbs [5] have introduced a definition of the cooperative rearranging region (CRR) as a subsystem, which can rearrange its configuration into another, independently of its environment upon a sufficient thermal fluctuation. The CRR volume is estimated from the Gibbs canonical distribution, $d\omega \sim \exp(-E(p,q)/k_B T) \, dp \, dq$, one of the most solid pillars of statistical physics. Since the temperature T is introduced from a heat bath by the zeroth law of thermodynamics, this distribution cannot represent a temperature fluctuation; all fluctuations are derived from energy fluctuations. In this case, the CRR volume is calculated from energy fluctuations (δE). According to Donth *et al* [6] the CRR volume

can be also calculated from the von Laue approach, which allows the temperature to fluctuate. Furthermore, it has been shown that the calorimetric experiments of glass transitions in confined geometries significantly exclude the Gibbs distribution from a treatment of cooperativity volume, whereas the von Laue treatment always gives reasonable results [6]. Thus, we have chosen to apply the Donth's approach in this work.

Each CRR can be considered as a thermodynamic system in metastable equilibrium with fluctuating variables having a Gaussian distribution. Each CRR has its own glass transition temperature T_α and its own relaxation time τ. In this approach, the relaxation time distribution is related to the glass transition distribution and $\langle T_\alpha \rangle$ is assumed to be the conventional glass transition of the sample noted T_g. This glass transition temperature distribution can be experimentally obtained, from temperature modulated differential scanning calorimetry (TMDSC) for example. According to Donth's approach, the CRR sizes were calculated for numerous organic polymers to study glass transition dynamics, the influence of physical ageing, crystallinity degree, etc [7–9]. As an example, it has been shown that the CRR size becomes anisotropic as a function of a specific molecular orientation induced by the drawing effect for drawn poly(ethylene terephthalate) (PET),

and the confinement effects due to the high crystallinity degree can be correlated to the CRR size decrease [9].

However, this approach was never applied to simple inorganic polymers, such as chalcogenide glasses, which owing to their simple structure can be considered in many cases as a model object. They are of a high purity; they possess structural parameters which have been evaluated over many years, even if some important discussions still remain. In our opinion, these advantages of simple inorganic polymers are not used enough, because there are a great number of unsolved questions regarding the organic polymers. First of all, it is not easy to analyse the influence of connectivity on the CRR size in organic polymers because of the complicated structure of monomer units. The other problem, which is usually present in organic polymer materials, is a relatively high concentration of impurities originating from the technological routes of their preparation (catalysts, etc). This hinders the analysis of most processes, since the impact of impurities on CRR features is not clear. Then, a relatively high number of possible conformations of monomer units with temperature creates additional problems during analysis.

Chalcogenide glasses of the As–Se system are relatively free of most of these disadvantages. This system is unique because it has the largest glass formation region among all the binary chalcogenides that allows one to obtain samples with preferentially linear one-dimensional (1D, consisting mostly of Se_n chains), two-dimensional (2D, caused by greater concentration of As) as well as three-dimensional (caused by shared $AsSe_{3/2}$ pyramidal units) structures [10–13]. So, the effect of connectivity on CRR size can be easily studied. The other advantage is that numerous data on the structure of As–Se glasses exist in the literature giving the possibility to link the CRR volume directly with the structural features of these materials [10–13]. Moreover, the physical ageing effect, which is associated with changes in CRR volume, is relatively well understood in As–Se chalcogenide glasses from the microstructural point of view [14, 15]. At last, the relatively simple structure of As–Se glasses allows application of different techniques with unambiguous interpretation of the obtained experimental results. All these arguments make the As–Se glass system a convenient model object for investigations of general trends in CRR volume depending on the structural features of polymer materials.

So, in the present paper, we will apply the CRR concept developed for organic polymers to study the processes occurring in As–Se chalcogenide glasses as a result of changes in the connectivity of a glass-forming backbone (by changing composition). The results will be analysed from the atomic-species and void-species points of view.

2. Experimental details

The samples of binary As_xSe_{100-x} ($x = 0, 10, 20, 30, 40, 45, 50, 53, 55$) were prepared by a conventional melt-quenching route in evacuated quartz ampoules from a mixture of high purity (99.999%) As and Se precursors. The furnace was rocked to obtain the most homogeneous melt. All ingots were quenched by switching off the furnace. The amorphous state

of the as-prepared chalcogenide glass was established visually by a characteristic conch-like fracture as well as by x-ray diffraction. Each sample was rejuvenated by heating above the glass transition temperature T_g, waiting in equilibrium at $T_g + 50$ K and subsequently cooling in the chosen regime at the same cooling rate, just before the calorimetric measurements to eliminate any thermal prehistory.

The samples are analysed using temperature modulated differential scanning calorimetry (TMDSC) of thermal analysis (TA DSC 2920). The specific heat capacities for each sample are measured using sapphire as a reference. The sample masses are chosen to be similar to the sapphire sample mass, i.e. approximately 20 mg. The TMDSC experiments are performed with an oscillation amplitude of 0.318 K, an oscillation period of 60 s and with a heating rate of 2 K min^{-1}. These experimental parameters correspond to the 'heat only' mode and give the best signal to noise ratio obtained with the apparatus used. From TMDSC, different signals can be obtained: the total heat flow and the apparent complex heat capacity C_p^* given by the following equation:

$$|C_p^*| = \frac{A_q}{A_\beta} \times \frac{1}{m} \qquad (1)$$

where A_q is the amplitude of the modulated heat flow, A_β the amplitude of the heating rate, and m the sample mass. Due to the phase lag φ between the calorimeter response function (i.e. the total heat flow) and the time derivative of the modulated temperature program, two components C_p' (the in-phase component) and C_p'' (the out-of-phase component) are calculated according to the following equations:

$$C_p' = |C_p^*| \cos \varphi \qquad (2)$$

$$C_p'' = |C_p^*| \sin \varphi. \qquad (3)$$

More details concerning the apparent complex heat capacity determination, especially the measured phase angle correction for contributions originating from heat transfer, are given in [16]. The C_p' versus temperature variations appear usually as an endothermic step and the C_p'' variations show a peak in the glass transition temperature region. The C_p'' peak maximum temperature is called T_α and corresponds to the glass transition temperature T_g in this work (see figure 1) ranging from 310 to 470 K depending on the composition. From C_p' and C_p'', the volume V_{T_g} of CRR at T_g could be estimated according to Donth's approach [5, 6]:

$$V_{T_g} = \frac{\Delta(1/C_V)}{\rho (\delta T)^2} k T_g^2 \qquad (4)$$

where the difference in reciprocal specific heat capacity $\Delta(1/C_V)$ is determined from TMDSC data

$$\Delta(1/C_V) \approx \Delta(1/C_P) = (1/C_P)_{\text{glass}} - (1/C_P)_{\text{liquid}}, \quad (5)$$

where $(\delta T)^2$ is the mean temperature fluctuation related to the dynamic glass transition of one CRR (figure 1); $\Delta(1/C_P)_{\text{glass}}$ and $\Delta(1/C_P)_{\text{liquid}}$ are estimated using C_p' spectra, as shown in figure 1; and ρ is a glass density.
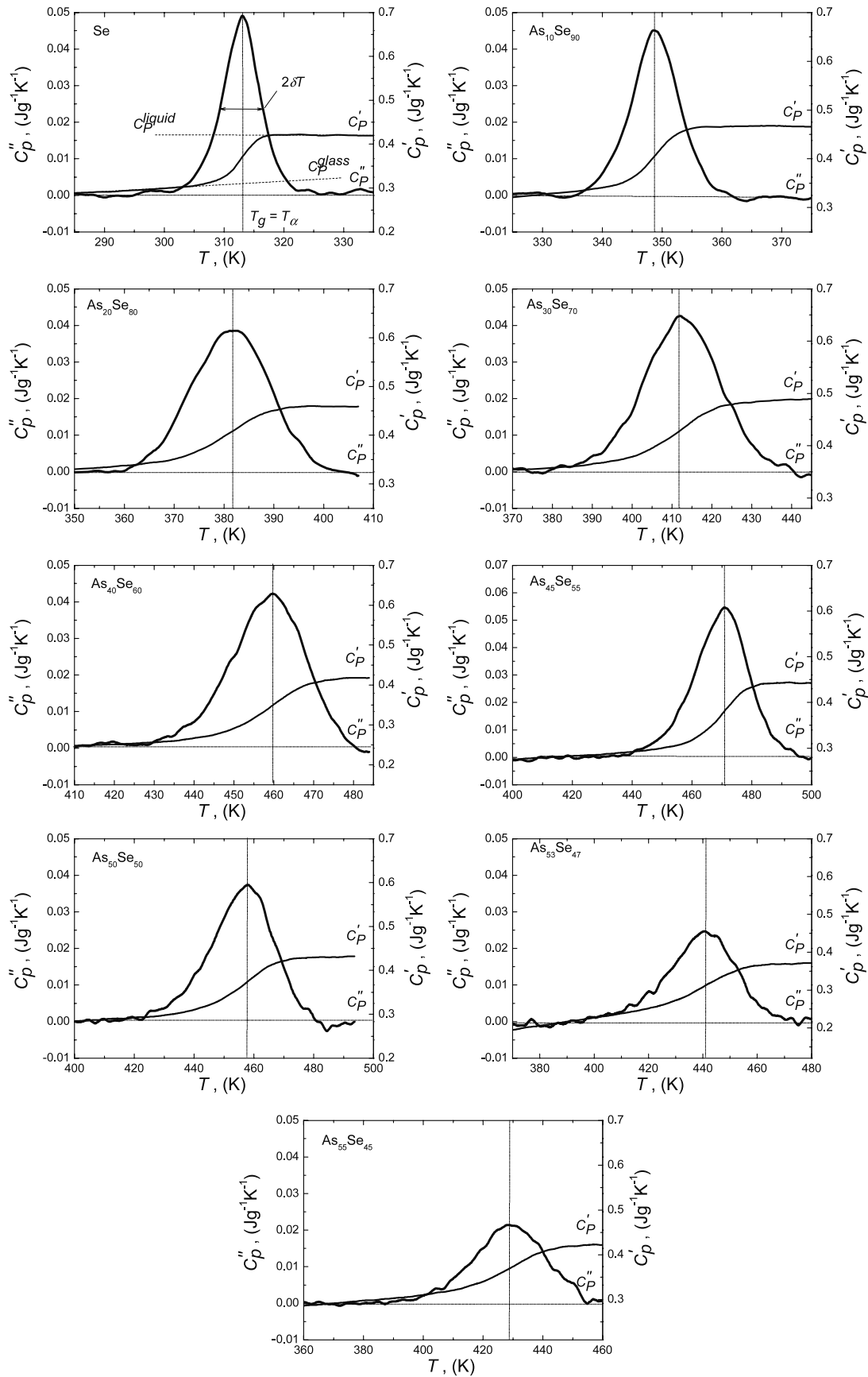
Figure 1. The C'_p and C''_p curves obtained by TMDSC after the rejuvenation procedure for the investigated As_xSe_{100-x} samples (oscillation amplitude 0.318 K, oscillation period 60 s, heating rate of 2 K min^{-1}); the first graph shows the method to determine quantities needed for the calculation of the characteristic CRR volume at the glass transition according to (4).
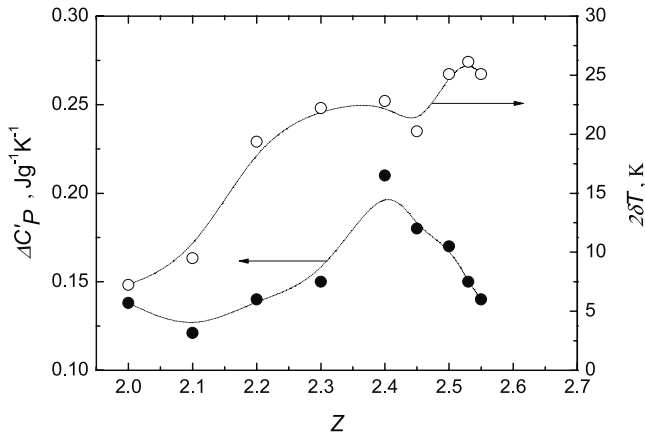
Figure 2. Compositional dependence of $\Delta C'_p$ and δT parameters used to calculate CRR volume in the investigated As–Se glasses. The lines are drawn as guide to the eyes.

Figure 3. Compositional dependence of CRR volume (a) and number of atoms within this volume (b) for the investigated As–Se glasses.

Then, the number of monomers N_m in one CRR can be estimated as:

$$N_m = \frac{\rho N_A V_{T_g}}{M} \qquad (6)$$

where N_A is the Avogadro number and M is the molar mass of one monomer unit.

The connectivity of the glass backbone for the investigated materials can be characterized (in the first approximation) by an average coordination number Z calculated as $Z = \left(\frac{\sum_r r n_r}{\sum_r n_r}\right)$ for the glass network constructed by n_r atoms having r bonds, $\sum_r n_r = N$ [17].

3. Results

Results of TMDSC measurements for the investigated samples are presented in figure 1 in the form of C'_p and C''_p dependences used to calculate CRR size. The C'_p values (0.12–0.21 J g^{-1} K^{-1}) were determined at T_α, as shown in figure 1, and found to be consistent with those observed previously by other authors [11]. The difference $\Delta C'_p$ exhibits a sharp maximum at $Z = 2.4$ (figure 2) corresponding to the As$_{40}$Se$_{60}$ stoichiometric composition. Accepting this value to be connected with difference in disorder between glassy and liquid states, we can conclude that the structure of stoichiometric glass is the most different from its undercooled liquid. However, it is known that this glass (As$_{40}$Se$_{60}$) is characterized by the absence of physical ageing, which is defined as spontaneous transition of the glassy state into a more thermodynamically favourable state closer to the equilibrium of undercooled liquid at a given temperature [2, 14, 17, 18]. Normally, it is associated with shrinkage of the glass network and should be directly proportional to this difference. So, not only the excess of enthalpy determines the ability of the system to undergo the relaxation processes, the connectivity of the glass backbone should be additionally taken into account. This can be done using the mean-field constraints theory [19], which considers the physical features of glass network depending on the number of constraints per atom n_c. According to this theory, only networks which have n_c less than a space
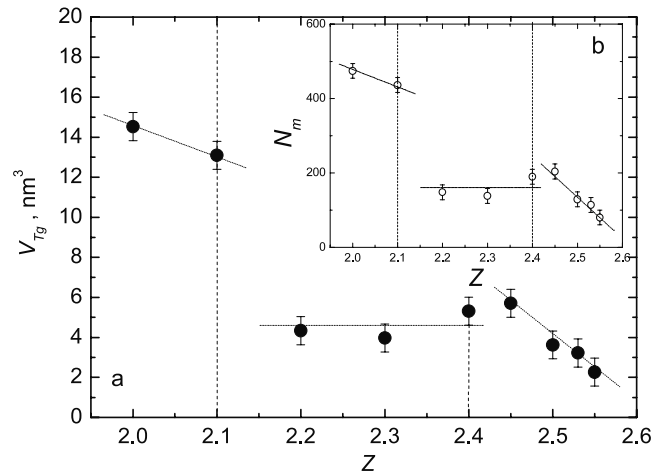
dimensionality ($n_c < 3$, for instance) could exhibit physical ageing effects at the temperatures below T_g. When $n_c = 3$, the glass network is optimally constrained and belongs to a so-called self-organized phase, characterized by the absence of physical ageing. In the case under consideration, only As$_{40}$Se$_{60}$ stoichiometric glass with $Z = 2.4$ was shown to have an optimally constrained network with $n_c = 3$ [20]. So, despite the significant $\Delta C'_p$ value for this composition, physical ageing at below-T_g temperatures is not possible in this glass due to the non-compressibility of the optimally constrained network. Further increase of As concentration ($Z > 2.4$) leads to the formation of an over-constrained stressed network with $n_c > 3$.

Increase of As content in the samples also causes the spreading of the C''_p peak, which is related to the spreading of glass transition range, expressed in $2\delta T$ values (figure 2). One can distinguish a possible plateau at a compositional range of approximately $Z \approx 2.3$–2.4.

4. Discussion

The CRR size calculated according to (4) for the investigated As–Se glasses and the number of atoms which participate in cooperative motions at T_g calculated according to (6) using density data of [21], are plotted as a function of average coordination number Z in figures 3(a) and (b), respectively. It is clearly seen that CRR volume and, consequently, the number of atoms in it, decreases after $Z = 2.1$ and 2.4 numbers. This is not the first experimental result which shows that average coordination numbers $Z = 2.1$ and 2.4 appear as threshold values separating the composition domain in three distinct zones. Various physical quantities, such as magnetic susceptibility, activation energy of conductivity, specific heat capacity, molar volume, and others [11, 13, 22–24] exhibited a well expressed extrema in compositional dependences at these points.

To understand this behaviour it is necessary to consider both the atomic-species and void-species structure of the investigated objects. It was shown recently that atomic-species structure of Se-rich As–Se glasses can be well described by

the 'chains crossing model' [12, 25]. Within this model, it is assumed that As atoms forming $AsSe_3$ pyramids are homogeneously distributed in the glass-forming network, with Se chains cross-linking these structural units. The mean number of Se atoms between them depends only on the glass composition: the greater the Se content, the longer the Se-based chains. The adequacy of this model to the real structure of Se-rich As–Se glasses was proved recently by solid-state nuclear magnetic resonance and x-ray photoelectron spectroscopy measurements [12, 25]. However, compositions with short Se_n chains ($n \leqslant 3$) have demonstrated a deviation of the bonds' statistical distribution from the 'chains crossing model' formalism of within ~5–7% [12].

In the case of Se-rich ($n > 3$) As–Se glasses, we can assume the formation of ring- or chain-like Se configurations (associated with *cis*- and *trans*-configurations of Se atoms in the chain) in their glass network depending on the length of Se_n chains. With this in mind, it is easy to predict a number of peculiarities in the structure of these materials depending on their average coordination number Z.

The minimum number of Se atoms necessary to form the ring-like configuration is related to the proper structural units of crystalline Se such as Se_8 crown-like rings [13]. As can be easily shown, the probability of forming Se_8 rings should vanish after $Z > 2.087$, when the n value becomes less than 8. This is the first Z value reported in the literature, which is characterized by extrema in compositional dependences of physical–chemical properties (often not precisely determined and varied in the range of $Z = 2.08 \pm 0.03$) [11, 13, 22–24]. For example, a sharp maximum in the paramagnetic component of magnetic susceptibility and activation energy of conductivity [22], an extremum in specific heat capacity [11], and a step in compositional behaviour of the intensity of positron lifetime component [26] was observed. It was demonstrated in the example of Ge–Se glasses [17, 24] that $Z \approx 2.1$ corresponds to the transition of the glass backbone from a quasi-linear 1D structure to the 2D polymeric network. So, a decrease in CRR volume observed at $Z \approx 2.1$ in our TMDSC experiment can be associated with an increase of general connectivity of the glass backbone when the whole structure of As–Se glasses becomes constructed by only polymeric Se_n chains (the probability for the existence of Se_8 crown-like molecules decreases rapidly) cross-linked by As atoms.

The well-known floppy to stress-free rigidity transition at $Z = 2.4$ together with the chemical phase transition is also reported as an extremum point in different compositional dependences for As–Se glasses [10, 13, 19, 22]. At this point, the structure of vitreous As_2Se_3 is supposed to be formed by directly linked corner-shared $AsSe_{3/2}$ pyramids and it is optimally constrained (rigid) [12, 13]. Therefore, observation of the peculiarity in the CRR volume dependence at $Z = 2.4$ (figure 2) is also not a surprise, depicting floppy-to-rigid changes in the connectivity of the As–Se glass backbone. However, the changes of CRR at $Z = 2.4$ are less drastic than at $Z = 2.1$. This is unexpected behaviour, because above $Z = 2.1$ the glass backbone is still considered as floppy, at the same time at $Z = 2.4$ it becomes rigid and optimally
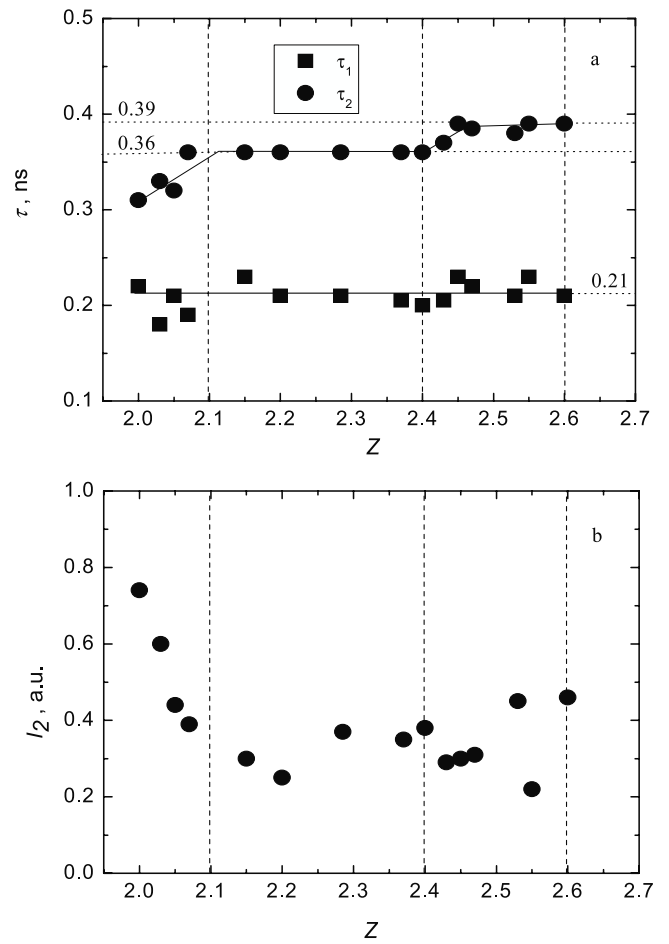
Figure 4. Compositional dependence of positron lifetimes τ_1 and τ_2 (a) and the intensity I_2 (b) of the τ_2 component in the fit responsible for open-volume defects in PALS data [26].

constrained with $n_c = 3$. So, more drastic changes of CRR volume were expected at the $Z = 2.4$ point. This forces us to assume that not only the connectivity determines a CRR size.

A complementary piece of information can be obtained from the analysis of void-species structure of As–Se glasses. One of the most suitable methods which can provide this information is positron annihilation lifetime spectroscopy (PALS) [27, 28]. It is grounded on the dependence of positron lifetime in the material on the existence of nanovoids free of the electronic density: the greater the open-volume defect, the greater the positron lifetime value (τ); the higher the concentration of these defects, the greater the intensity of the τ component associated with them in the fit of the experimental curve (if saturation of positron trapping in these defects or chemistry effects are excluded) [27]. PALS data for the as-prepared As–Se glasses measured at room temperature are presented in figure 4 as reconstructed from the publication of Alekseeva *et al* [26]. The initial PALS signal was fitted by two components with τ_1 and τ_2 lifetimes and I_1 and I_2 intensities, respectively [26]. The τ_1 component was related to the lifetime of positrons in the defect-free bulk material (crystalline counterpart, in the first approximation), the τ_2 component was associated with open-volume defects
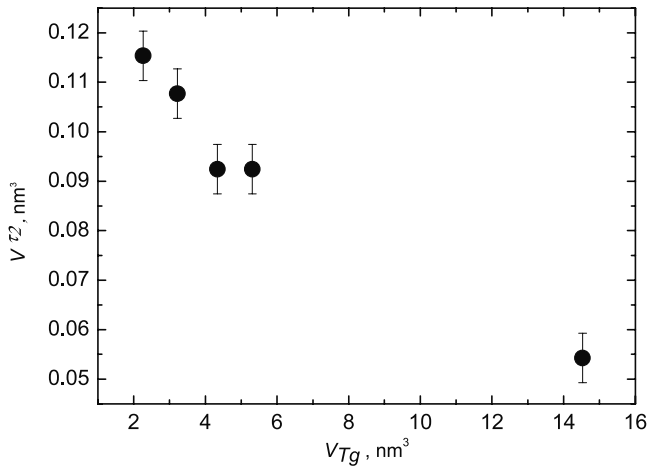
Figure 5. Correlation dependence between the size of open-volume defects (V^{τ_2}) calculated using PALS data of [26] and CRR size (V_{T_g}) determined using TMDSC data at T_g.

within the glass network. Two steps in the compositional dependence of τ_2 values can be distinguished from figure 4 (taking into account a reasonable accuracy of PALS data for the As–Se system [27]) at $Z \approx 2.1$ and 2.4, which is consistent with the peculiarities observed at these points by other researchers [13, 22]. Using Jensen's approach [28] developed for As_2Se_3, it is possible to estimate the size of open-volume defects at room temperature in the investigated materials using these PALS data:

$$V^{\tau_2} \ (\text{Å}^3) = (\tau_2 \ (\text{ns}) - 0.2389)/0.0013. \qquad (7)$$

Taking into account the small coefficient of thermal expansion for the studied materials ($<4 \times 10^{-5} \ K^{-1}$) [21], we can assume negligible changes in V^{τ_2} when approaching T_g, where the CRR volume was calculated according to equation (4).

To have a correct compositional dependence, formula (7) should be used with some precautions. First of all, it predicts the constant value of τ_1—a component related to the lifetime of positrons in the defect-free bulk material (As_2Se_3 crystal, for instance). So, from the experimental data of Alekseeva *et al* [26] we have chosen for analysis only the points with $\tau_1 = 0.21 \pm 0.01$ ns, assuming no compositional dependence for τ_1, as could be arbitrarily presumed from figure 4. Then, we have selected the compositions that directly correspond to the investigated objects with calculated CRR. Doing so, we obtained the dependence of CRR volume on V^{τ_2} as shown in figure 5. Thus, we can speculate that the greater the size of individual open-volume defect, the smaller would be the CRR size. The open-volume defects of 80–100 Å^3 in size (0.08– 0.1 nm^3) can be considered as crucial ones for the existence of CRR volumes in As–Se glasses greater than 4 nm^3 (more than $\sim$200 atoms in the CRR region, figure 3(b)).

In principle, it is possible to compare the relative concentration of these defects having the intensity I_2 of the τ_2 component. However, this may lead to a misleading conclusion, since I_2 depends considerably on the spatial distribution of the open-volume defects. If the distance

between trapping centres is comparable with the diffusion length of thermalized positrons, the intensity of the component responsible for the bulk annihilation (I_1, for instance) decreases rapidly, positron trapping being saturated in these centres. In this case I_2 will not reflect the true concentration of trapping centres. However, this should not affect the τ_2 values considerably and, consequently, the estimated size of open-volume defects. From comparison of I_2 (figure 4(b)) with CRR size (figure 3) it can be inferred that small-size (up to 80–100 Å^3 i.e. 0.08–0.1 nm^3) open-volume defects even in significant concentrations ($I_2 \sim 70\%$ for vitreous Se) do not break CRR in As–Se glasses as effectively as larger open-volume defects do with much smaller concentration. So, the determining factor for CRR size in As–Se glasses is their dimension, but not concentration (in meaningful values, of course).

It should be noted here, that the PALS technique is sensitive only to a limited number of open-volume defects in glasses (usually nanovoids) and the cross-section of annihilation depends considerably on the potential well associated with each of them (such as, for example, neutral or negatively charged vacancies). The TMDSC technique is an integral method sensitive to all structural imperfections. This may complicate the present consideration concerning the PALS data, which can be accepted only to some extent determined by the limitation of the PALS technique.

5. Conclusions

It is shown by the present TMDSC experiment that compositional dependence of the CRR volume size exhibits peculiarities near points $Z = 2.1$ and 2.4 in As–Se glasses, depicting a general connectivity of the glass backbone, which, in turn, is determined by the length of Se_n chains between pyramidal structural units. The drastic changes of CRR size near the point $Z = 2.1$ cannot be explained by only the connectivity criterion. On the basis of the PALS data obtained earlier, the hypothesis has been put forward that the appearance of large-size nanovoids in the structure of polymer materials additionally leads to a decrease in CRR average size.

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