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Stoichiometric arsenic sulphoselenides as testing probes for positron trapping in chalcogenide glasses

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Positron annihilation lifetime (PAL) measurements are performed for stoichiometric glassy arsenic sulphide g-As_2S_3 and selenide g-As_2Se_3 in order to probe the corresponding model of positron trapping. An ORTEC spectrometer with ^{22}Na source placed between two sandwiched glass samples was used in our experiments, the obtained spectra being treated with LT computer program. Two identical samples of g-A_2S_3 and g-As_2Se_3 of about ~1.5 mm in thickness prepared from high-purity elemental constituents by conventional melt-quenching route and additionally annealed near glass transition to avoid the inner stressed regions were tested. It is shown that two-state positron trapping model is valid for both glasses, the process of positron trapping being saturated in extended free-volume defects like to atomic vacancies and their agglomerates. Despite difference in the character of nanovoid radius distribution estimated theoretically for g-As_2S_3 and g-As_2Se_3, they have very close average free volumes resulting in the observed similarity of PAL data. But, in contrast to g-As_2Se_3, which has at least three sets of nanovoids centered near ~1.5 Å, ~2.3 Å and ~2.9 Å, only two sets of nanovoids centered near ~1.3 Å and at ~2.8 Å are proper to g-As_2S_3 giving only one variant of fitting.

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1. Introduction

Nowadays, an adequate understanding of correlation between structure and physical-chemical properties of chalcogenide glasses (ChG), representing themselves as chemical compounds of IV-V-group elements with chalcogen atoms (S, Se, Te, but not O) prepared by conventional melt-quenching [1], is still in a sphere of sharp scientific and commercial interests for scientists and numerous known electronic firms from all over the world [1]. The atomic-species structure or spatial ordering arrangement in atomic positions is typically taken as main determinant for their properties [2]. But atomic structural knowledge alone is not quite exhaust for this purpose. Indeed, for instance, the known free volume concept introducing numerical measure of free volume through atomic compactness plays a key role in the interpretation of compositional features of fundamental properties as well as induced physical phenomena in different ChG [3-7]. The source of this concept is essential excess of free volume for ChG in comparison with thermodynamically equilibrium crystal of the same chemical composition [2], and this is a proper feature for the structure of any disordered solids due to their metastability. The main kinds of internal free-volume nanovoids in ChVS are connected with electron density distribution of covalent chemical bonds within some atomic configurations [8], fluctuations of structural fragments frozen near glass transition [9] and geometrical inconsistencies of different glass-forming structural units [10,11].

Therefore, the real structure of ChG should be studied not only at atomic-species, but also at void-species level. That is why the positron annihilation lifetime (PAL) spectroscopy, the method which is especially sensitive to free-volume distribution in solids [12], is considered to be a quite promising tool in such application.

As a rule, the measured PAL data are treated within a well-known two-state positron trapping model considering one type of extended free-volume positron traps in the tested material [7,12]. Nevertheless, being applied to topologically disordered solids without translational symmetry such as ChG, we have a real problem with correct interpretation of these data because of some uncertainties in PAL parameters and possible input of additional channels of positron annihilation not foreseen within this model. To resolve correctly this problem, we should consider the real content of free volume and its special distribution in the inner structure of the chosen ChG.

The main aim of this work is to develop a meaningful interpretation of PAL characteristics treated within two-state positron trapping model for two kinds of ChG of the same layer-like structural type, but having different nanovoid topology – the stoichiometric glassy arsenic sulphide g-As_2S_3 and selenide g-As_2Se_3.

2. Experimental

Two identical samples of v-A_2S_3 and g-As_2Se_3 of about ~1.5 mm in thickness prepared from high-purity elemental constituents by melt-quenching technique [2]

and additionally annealed near glass transition to avoid inner stressed regions were used in our experiments.

The PAL measurements were performed with an ORTEC spectrometer using ^{22}Na source placed between two sandwiched ChG samples [12]. The obtained spectra were treated with LT program [13], the best results corresponding to two-component fitting procedure. We used 5 measured PAL spectra for each pair of ChG samples, they differing by a total number of counts or, in other words, the ordinary annihilation evens in the range of 800000-1200000. Each of these spectra was multiply treated owing to slight changes in the number of final channels, background of annihilation and time shift of the spectrum. Firstly, the parameters of PAL spectrum with long-lived part were calculated and, then, the number of final channels was reduced in such a way to cut off the long-lived annihilation background. This procedure was a quite reasonable one, since there were no long-lived lifetime components with $\tau > 1$ ns in the measured PAL spectra. Then, the variance of FIT was taken into account to compare the obtained results. This parameter was determined as statistically weighted least-squares deviation between experimental points and theoretical curve. Only results with FIT values, which were quite close to 1.0 (the optimal FIT deviates from 0.95 up to ~1.1-1.2 [12]), were leaved for further treatment. At the next stage, this FIT and determined PAL characteristics were controlled in dependence on the background of annihilation and time shift of PAL spectrum, the results showing slight changes being selected. It should be noted that source correction and spectrometer resolution function were kept unchangeable for all PAL spectra.

By accepting that two-state positron trapping model [7,12] is valid for the studied ChG, the numerical parameters of this model were calculated using τ_1, τ_2, I_1 and I_2 (within considered model, $I_1 + I_2 = 1$) values obtained with applied fitting procedure. The bulk positron lifetime τ_b, average positron lifetime $\bar{\tau}$ and positron trapping rate κ_d were calculated, respectively, as [12]:

$$\tau_b = \left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1} = \frac{\tau_1 \tau_2}{I_1 \tau_2 + I_2 \tau_1}, \quad (1)$$

$$\bar{\tau} = I_1 \tau_1 + I_2 \tau_2, \quad (2)$$

$$\kappa_d = I_2 \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right). \quad (3)$$

In addition, the difference $(\tau_2 - \tau_b)$ was accepted as a size measure for extended defects where positrons are trapped in terms of equivalent number of monovacancies, as well as the τ_2/τ_b ratio was accepted as parameter corresponding to the nature of these defects [12].

3. Results

Two-component fitting parameters of LT computer program, describing positron annihilation in g-As_2S_3 and g-As_2Se_3 within two-state positron trapping model are gathered in Table 1. We established that two groups of fitting parameters undistinguishable in FIT because of close $\bar{\tau}$ and τ_b (the systematic error was ±0.01 ns in positron lifetime and ±0.01 in component intensity) are character for g-As_2Se_3 with very close probability. For simplicity in a further consideration, they are denoted as I-As_2Se_3 and II-As_2Se_3, respectively. In the case of g-As_2S_3, only one group of fitting parameters was obtained, it being practically identical with one of the groups for g-As_2Se_3 (see Table 1).

4. Discussion

In 1994, K. O. Jensen et al. [14] obtained the PAL characteristics for g-As_2Se_3 water-ice-quenched from 650^{o}C, which were in obvious contradiction to the previous data of O. K. Alekseeva et al. [15-18].

The short positron lifetime τ_1 was as high as 0.29 ns, while the intensity of the second component I_2 jumped up to 0.75. To explain these experimental results, the theoretical calculations of positron lifetimes for different kinds of vacancy-type defects in crystalline (orthorhombic) c-As_2Se_3 were performed on the basis of Puska's positron trapping model [12,19].

It was assumed that not native point-type charged defects, but only extended vacancy-type voids associated with 25-100 Å^3 free volumes were responsible for positron trapping in both c-As_2Se_3 and g-As_2Se_3.

The numerical values of positron lifetimes τ (in ns) were found to be in linear dependence on free volume V (in Å^3):

$$\tau \cong 0.240 + 0.0013V. \quad (4)$$

Therefore, contrary to the previous interpretation of O. K. Alekseeva et al. [16-18], these results were described in terms of saturated positron trapping in extended free-volume defects.

Table 1. Two-state positron trapping characteristics of g-$As_2S(Se)_3$ calculated with LT computer program [13].

Sample	Fitting parameters			Component input		Positron trapping modes				
	τ_1 (ns)	τ_2 (ns)	I_2 (a.u.)	$\tau_1 I_1$ (ns)	$\tau_2 I_2$ (ns)	$\tau_{av.}$ (ns)	τ_b (ns)	κ_d (ns^{-1})	$\tau_2 - \tau_b$ (ns)	τ_2/τ_b
I-As_2Se_3	0.20	0.37	0.60	0.08	0.22	0.30	0.28	1.31	0.09	1.32
II-As_2Se_3	0.225	0.385	0.50	0.11	0.19	0.30	0.285	0.91	0.10	1.35
As_2S_3	0.20	0.375	0.61	0.08	0.23	0.31	0.28	1.51	0.095	1.34

However, despite a number of significant differences, it was non-ambiguously adopted a fully identical origin for these positron traps in chalcogenide crystals and glasses.

Our PAL experiments with g-As_2Se_3 (Table 1. see also references [20-22]) testify rather in a favour of the early Alekseeva's data [16-18]. However, we obtained two close groups of results for g-As_2Se_3 differing only by positron trapping rate κ_d.

To understand better the above feature in PAL data for g-As_2Se_3 as well as the observed similarity in PAL spectra for g-As_2S_3 and g-As_2Se_3, let's consider the proper structural models describing free volume distribution within their glass-forming networks [23]. These models are significantly different from numerical view in respect to different content of average free volume in both ChG. But we have easily balanced them by accepting the access in the volume of glass in respect to the corresponding crystal of the same chemical composition as a measure of total free volume character to ChG. With known numerical parameters for glassy-like and crystalline As_2S_3 and As_2Se_3 [2], this additional free volume can be estimated as 2.28 $Å^3$/atom for g-As_2S_3 and 1.30 $Å^3$/atom for g-As_2Se_3. The diagram on Fig. 1a and 1b are arranged in such a way to keep just this ratio (2.28:1.30) in the sum of total free volume in these ChG.

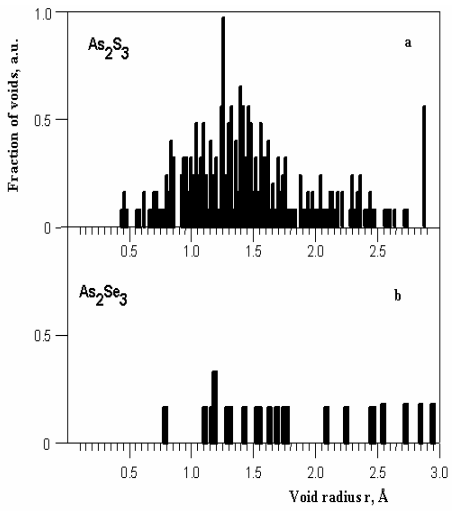

Fig. 1. Nanovoid radius/volume distribution for 800-atoms model of g-As_2S_3 (a) and 146-atoms layer-biased structural model of g-As_2Se_3 (b) [23].

Two groups of results proper to g-As_2Se_3 can be explained by taking into account free-volume distribution in this ChG within layer-biased model shown in Fig. 1b [23]. This 146-atoms model contains at least three sets of free-volume voids centred near $\overline{r_1} \approx 1.5$ Å, $\overline{r_2} \approx 2.3$ Å and $\overline{r_3} \approx 2.9$ Å denoted by arrows, as well as alone line with ~0.7 Å radius (all lengths are given in spherical approximation). These structurally intrinsic free-volume voids of nanoscale sizes (nanovoids) can be effective traps for positrons with character lifetimes determined by Eq. (4) in dependence on their corresponding trapping rates, Eq. (3). Consequently, two separate components in the experimentally measured PAL spectra of g-As_2Se_3 may differ, resulting from different inputs of separate free-volume nanovoids. Presumably, just this feature leads to the above discrepancy in the experimentally measured PAL data.

As one of the most essential conclusion, it should be emphasises that, in accordance to the Eq. (4), the numerical value of the longest positron lifetime associated with nanovoids centred near $\overline{r_3} \approx 2.9$ Å within the above layer-biased model of g-As_2Se_3 [23] corresponds exactly to $\tau = 0.37$ ns. This defect-related lifetime can be changed within 0.35 - 0.38 ns range by accepting that three kinds of nanovoids with 2.8, 2.9 and 3.0 Å radii lay in this void radius range (see Fig. 1). So it can be assumed, that just this kind of free-volume nanovoids in g-As_2Se_3 has the highest value of κ_d, tending the overall process of positron trapping to saturation with constant value of defect-related lifetime τ_2 close to 0.37 - 0.38 ns and slightly-changed short lifetime τ_1 in dependence on preferential inputs from other positron trapping channels.

The both groups of results for g-As_2Se_3 has τ_2/τ_b ratio close to 1.3, which testified that corresponding positron-trapping centres are of the same type, being, most probably, as large as di- or/and tri-vacancies [12]. At the same time, the second group contains the greater $\tau_2 = 0.385$ ns and, consequently, the greater $(\tau_2 - \tau_b)$ difference. So the corresponding defects have the greater free volume. Within the above layer-biased model [23], it can be supposed that nanovoids with 2.9 Å radius are responsible for the first PAL signal having $\tau_2 = 0.37$ ns and $\kappa_d = 1.3$ ns^{-1}, while ones with

3.0 Å radius are responsible for the second PAL signal with $\tau_2 = 0.385$ ns and relatively reduced $\kappa_d = 0.9$ ns^{-1}. By using Eq. (4), the corresponding defect-related positron lifetimes τ_2 can be estimated as 0.37 and 0.38 ns for the above groups of nanovoids, respectively, that is in a good accordance to the experimentally measured τ_2 values given for g-As_2Se_3 in Table 1.

As to the input of the first PAL component in the overall process of positron trapping, it is a determinant of average electron density distribution reflected structural compactness of a whole glass-forming network. This parameter is difficult for strict numerical determination using nanovoid radius distribution shown in Fig. 1b. We can only more or less roughly estimate this value will be quite close to 1.2 Å, where a relatively intensive separate line can be distinguished.

In the case of g-As_2S_3, the character of free-volume distribution changes significantly as it follows from Fig. 1a. The nanovoids in this ChG are of two types, the first of them being peak-centered near 1.2 - 1.4 Å with a character bell-like envelope stretched from 0.5 to 2.5 Å and the second giving alone line of relatively high intensity at 2.87 Å.

Of course, the positron trapping is saturated in g-As_2S_3 too, this process being caused by a large number of nanovoids with a character radius of 2.87 Å. By assuming that Eq. (4) leaves valid in g-As_2S_3 (that seems to be quite reasonable because of the same structural type for both ChG under consideration), the corresponding τ_2 value is expected to be close to 0.37 ns in full respect to the measured $\tau_2 = 0.375$ ns (see Table 1). But, in contrast to g-As_2Se_3, there are no other nanovoids in g-As_2S_3, which will be competitive with this kind of nanovoids. Therefore, only one variant of fitting is proper to g-As_2S_3.

The average free volume within a whole glass-forming network in g-As_2S_3 can be roughly estimated as maximum of bell-like curve (1.2 - 1.4 Å) shown in Fig. 1a. This value is quite close to relatively intense separate line near 1.2 Å in g-As_2Se_3 (see Fig. 1b). So, despite difference in the character of nanovoid radius distribution in these ChG, they have very close values of minimal average free volumes which can be distinguished within their glass-forming networks. As a result, the input of the first PAL component in these ChG is similar too as it testifies from Table 1. It is quite understandable, that this conclusion should be accepted with some precaution because of principal difference in the character of free volume distribution in g-As_2Se_3 and g-As_2S_3 (as it seen from Fig. 1a and 1b), that can lead to additional mismatch in the corresponding values of positron trapping rates of free-volume defects.

Finally, we must mention that recently it was shown that self-organization can act in chalcogenide films and bulk glasses [24-26]. This phenomenon leads to the realization of nano-structural clustering and nano-scale molecular phase separation in the disordered network [25,27]. As a consequence the void distribution will be different from the case of ideal continuous random network considered in modelling. It should be noted that in the case of mixed As_2S_3-As_2Se_3 ChG, the final result of PAL measurements is expected to be significantly different from both boundary components. This complication will be because of mixing, at least, three principally different types of nanovoids possible in these samples – separate nanovoids forming individual sets as in the case of g-As_2Se_3 (see Fig. 1b), nanovoids centred around bell-like curve and nanovoids of alone line as in the case of g-As_2S_3 (see Fig. 1a).

5. Conclusion

Despite difference in the character of nanovoid radius distribution estimated theoretically for g-As_2S_3 and g-As_2Se_3, they have very close average free volumes resulting in a similarity of the measured PAL data. But, in contrast to g-As_2Se_3, which has at least three sets of nanovoids centered near ~1.5 Å, ~2.3 Å and ~2.9 Å, only two sets of nanovoids at ~1.3 Å and at ~2.8 Å are proper to g-As_2S_3 giving only one variant of fitting.

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