

# Radiation-induced extended free-volume defects in mixed ternary Ge-As/Sb-S glasses studied with PALS technique

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Under-coordinated topological defects caused by high-energy  $\gamma$ -irradiation can be a reason for significant changes in positron annihilation lifetime spectra of multicomponent chalcogenide glasses within ternary Ge-As(Sb)-S systems. In case of negatively-charged sulphur and arsenic atoms, the excess of free volume is quite enough to produce detectable input in defect-related channel of positron trapping, while under-coordinated negatively-charged germanium atoms are non-detectable with this technique because of low value of associated free volumes.

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## 1. Introduction

Chalcogenide glasses (ChG) are known can be effectively modified with external influences such as high-energy  $^{60}\text{Co}$   $\gamma$ -irradiation [1-3]. This unique ability has no exhaustive explanation up to now, but probably it is associated with high steric flexibility proper to a glassy-like network with low average coordination (chalcogen S, Se and Te atoms are always two-fold-coordinated in normal uncharged state), relatively large internal free volume proper to all melt-quenched disordered solids like glasses and specific lp-character of chalcogen-related electronic states localized at a valence-band top [1].

It was shown previously that measurable changes of physical-chemical properties are mainly caused by specific structural defects proper to ChG, which appear in the form of negatively charged over- and under-coordinated atomic pairs having anomalous number of nearest neighbours [1,4-9]. In respect to their nature, these defects often called coordination topological defects appear in a glass-forming network in the result of covalent bond switching. One bond is destroyed by external factor, but another one appears in its vicinity keeping overall covalent bonding through whole bulk [1,7]. This process is accompanied by structural relaxation at the level of intermediate range-ordering with an appearance of additional free volume near negatively-charged under-coordinated atoms [8,9]. The appeared free-volume nanovoids contain two components, the first one being due to lack of one (destroyed) covalent chemical bond and the second one being due to bond-destroying structural relaxation between directly non-linked atoms (atomic displacements to stabilize a new bond configuration within glass-forming network) [10-13]. So these negatively-charged under-coordinated extended defects can be identified experimentally with nanovoid-sensitive technique.

Positron annihilation lifetime spectroscopy (PALS) is known to be one of the most suitable tools for this purpose [14].

In spite of their structural-chemical specificity, the PALS-detectable extended defects vary significantly even in binary ChG systems like to As-S, As-Se, Ge-S, Ge-Se [10]. Moreover, to identify correctly PALS characteristics of these defects, the specific features of initial free volume distribution in ChG should be accepted in respect to the known structural models. At the present, these models are more or less developed for simple stoichiometric binary  $\text{As}_2\text{S}(\text{Se})_3\text{ChG}$  [15,16].

In the case of mixed ChG with 2-, 3- and 4-fold coordinated atoms (such as S, As and Ge, respectively), three different types of coordination defects are possible with different probabilities in dependence on glass composition –  $\text{S}_1^-$ ,  $\text{As}_2^-$  and  $\text{Ge}_3^-$  (the upper and lower indexes mean electric charge state and local atomic coordination or number of directly covalent-bonded neighbouring atoms, respectively) [10]. This work is aimed to testify the above extended defects in mixed ternary ChG of Ge-As-S and Ge-Sb-S systems with stoichiometric and non-stoichiometric cut-sections using PALS results treated within known one-state (non-defect) and two-state positron trapping models [14,17].

## 2. Experimental

The bulk ChG samples of ternary Ge-As-S and Ge-Sb-S systems were prepared by conventional melt-quenching route [8]. The chosen glass compositions were stoichiometric and non-stoichiometric ones in respect to germanium sulphide allowing wide deviation in average coordination number  $Z$  (the number of covalent bonds per one atom of glass-forming structural unit provided all

covalent bonds are fully saturated due to known 8-N rule [8]:

stoichiometric  $(As_2S_3)_{0.6}(GeS_2)_{0.4}$ ,

stoichiometric  $(As_2S_3)_{0.4}(GeS_2)_{0.6}$ ,

stoichiometric  $(As_2S_3)_{0.1}(GeS_2)_{0.9}$ ,

non-stoichiometric  $(As_2S_3)_{0.6}(Ge_2S_3)_{0.4}$ ,

non-stoichiometric  $(As_2S_3)_{0.4}(Ge_2S_3)_{0.6}$ ,

non-stoichiometric  $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$ ,

stoichiometric  $(Sb_2S_3)_{0.2}(GeS_2)_{0.8}$ ,

non-stoichiometric  $(Sb_2S_3)_{0.375}(Ge_2S_3)_{0.625}$ ,

non-stoichiometric  $(Sb_2S_3)_{0.125}(Ge_2S_3)_{0.875}$ .

After synthesis, all ingots were sliced into 1.0-1.5 mm thick disks with 10-12 mm diameter and outer surfaces polished to a high optical quality.

To produce a detectable amount of extended defects, the prepared As-contained ChG were irradiated by  $\gamma$ -quanta to the dose of 2.8 MGy, while Sb-contained ChG were irradiated to 3.0 MGy dose. This treatment was performed in a stationary radiation field created in a closed cylindrical cavity by concentrically maintained  $^{60}Co$  sources (the average energy of  $\gamma$ -quanta was 1.25 MeV).

The PALS measurements were performed with an ORTEC spectrometer using  $^{22}Na$  source placed between two sandwiched ChG samples [10-13]. The obtained data were treated with LT computer program [18], the best results corresponding to one- or two-component fitting procedures. In the latter case (within two-state positron trapping model [14,17]), the numerical values of trapping parameters (bulk positron lifetime  $\tau_b$ , average positron lifetime  $\tau_{av}$  and positron trapping rate  $\kappa_d$ ) were calculated using short and long positron-trapping lifetimes  $\tau_1$  and  $\tau_2$ , as well as component intensities  $I_1$  and  $I_2$  ( $I_1 + I_2 = 1$ ) [14,17]:

$$\tau_{av} = I_1\tau_1 + I_2\tau_2, \quad (1)$$

$$\kappa_d = I_2 \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right). \quad (2)$$

In addition, the difference ( $\tau_2 - \tau_b$ ) was accepted by us as a size measure for positron-trapping extended defects in terms of equivalent number of singlet vacancies, as well as the  $\tau_2/\tau_b$  ratio was accepted as parameter corresponding to the nature of the created extended defect [14]. The defect-free (bulk) positron lifetime  $\tau_b$  was calculated as

$$\tau_b = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1} = \frac{\tau_1\tau_2}{I_1\tau_2 + I_2\tau_1}. \quad (3)$$

### 3. Results and discussion

PALS characteristics describing positron annihilation in the studied ChG before and after  $\gamma$ -irradiation are gathered in Table 1 and 2, respectively.

Table 1. Positron trapping characteristics of non-irradiated ChG.

ChG composition	Z	Fitting parameters			Positron trapping modes	
		$\tau_1$ ns	$\tau_2$ ns	$I_2$ a.u.	$\tau_{av}$ ns	$\kappa_d$ ns <sup>-1</sup>
$(As_2S_3)_{0.6}(GeS_2)_{0.4}$	2.48	0.36	-	-	0.36	-
$(As_2S_3)_{0.4}(GeS_2)_{0.6}$	2.53	0.36	-	-	0.36	-
$(As_2S_3)_{0.1}(GeS_2)_{0.9}$	2.63	0.36	-	-	0.36	-
$(As_2S_3)_{0.6}(Ge_2S_3)_{0.4}$	2.56	0.33	-	-	0.33	-
$(As_2S_3)_{0.4}(Ge_2S_3)_{0.6}$	2.64	0.34	-	-	0.34	-
$(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$	2.72	0.24	0.39	0.57	0.32	0.9
$(Sb_2S_3)_{0.375}(Ge_2S_3)_{0.625}$	2.65	0.18	0.39	0.43	0.27	1.3
$(Sb_2S_3)_{0.125}(Ge_2S_3)_{0.875}$	2.75	0.17	0.39	0.51	0.28	1.6

In case of non-irradiated stoichiometric  $As_2S_3$ - $GeS_2$  ChG, only one PALS component with  $\tau_1 = 0.36$  ns can be distinguished whichever the sample composition. After  $\gamma$ -irradiation, the second long-lived PALS component having  $\tau_2$  close to 0.39 ns appears, this component being attributed to free-volume extended defects with trapping rate  $\kappa_d$  increasing with Ge content in the studied ChG.

Table 2. Positron trapping characteristics of  $\gamma$ -irradiated ChG.

ChG composition	Z	Fitting parameters			Positron trapping modes	
		$\tau_1$ ns	$\tau_2$ ns	$I_2$ a.u.	$\tau_{av}$ ns	$\kappa_d$ ns <sup>-1</sup>
$(As_2S_3)_{0.6}(GeS_2)_{0.4}$	2.48	0.28	0.39	0.33	0.32	0.3
$(As_2S_3)_{0.4}(GeS_2)_{0.6}$	2.53	0.29	0.39	0.38	0.33	0.4
$(As_2S_3)_{0.1}(GeS_2)_{0.9}$	2.63	0.28	0.39	0.47	0.33	0.5
$(As_2S_3)_{0.6}(Ge_2S_3)_{0.4}$	2.56	0.27	0.39	0.42	0.32	0.5
$(As_2S_3)_{0.4}(Ge_2S_3)_{0.6}$	2.64	0.34	0.39	0.45	0.33	0.5
$(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$	2.72	0.24	0.39	0.67	0.34	1.2
$(Sb_2S_3)_{0.375}(Ge_2S_3)_{0.625}$	2.65	0.18	0.40	0.42	0.28	1.2
$(Sb_2S_3)_{0.125}(Ge_2S_3)_{0.875}$	2.75	0.17	0.40	0.46	0.28	1.3

In case of non-irradiated non-stoichiometric  $As_2S_3$ - $Ge_2S_3$  ChG, one PALS component with lower  $\tau_1 = 0.33$ - $0.34$  ns can be distinguished for both As-enriched samples, while in Ge-enriched  $(As_2S_3)_{0.2}(Ge_2S_3)_{0.8}$  sample two PALS components appear. After irradiation, all samples of this system demonstrate two PALS components with similar  $\tau_2$  close to 0.39 ns. But, in contrast to As-enriched ChG samples having relatively low trapping rate  $\kappa_d$  (less than  $0.5$  ns<sup>-1</sup>), Ge-enriched sample shows higher trapping rate  $\kappa_d = 1.2$  ns<sup>-1</sup>.

Whichever stoichiometry, all irradiated As-contained ChG allowing two-component deconvolution procedure demonstrate very similar ( $\tau_2 - \tau_b$ ) difference close to 0.07-0.08 ns and ratio  $\tau_2/\tau_b \cong 1.3$  character for bi- and/or tri-

vacancies [14]. It means that in all these cases the preferential positron traps are of the same nature.

At the same time, Sb-contained ChG of both stoichiometric and non-stoichiometric cut-sections show two-component PALS results either before or after irradiation. There were no significant differences in the second PALS component caused by  $\gamma$ -irradiation as it testified from a comparison of positron trapping modes in Table 2. The character ( $\tau_2 - \tau_b$ ) differences in Ge-Sb-S ChG are greater in comparison to Ge-As-S ChG being at the level of 0.15 ns and  $\tau_2/\tau_b$  ratio are close to 1.6-1.7 testifying in a favour of more extended nature of existing positron-trapping defects (probably, tri- and tetra-vacancies or even vacancy-like complexes [14]).

The above results testify that negatively-charged under-coordinated extended defects with an associated free volume differ significantly in As- and Sb-contained ChG within chosen ternary systems. To explain this difference, let's consider the corresponding extended defects more precisely in dependent on ChG composition.

It is well known that some internal nanoscale voids (nanovoids) always appear in chemical compounds containing chalcogen S, Se, Te and/or pnictogen P, As, Sb, Bi atoms due to specificity in electron density distribution of covalent bonds around them [10,19]. Sometimes, this kind of free volume in ChG is called the bond-free solid angle volume as it proposed by M. Kastner [19]. This feature is well illustrated in Fig. 1, 2, 3 for electrically-neutral two-, three- and four-fold coordinated atoms, respectively (these atomic configurations in ChG can be conditionally marked as  $S_2^0$ ,  $As_3^0$  and  $Ge_4^0$ , the upper index denotes charged state and lower one denotes neighbouring directly covalent-bonded atomic coordination).

By accepting that two covalent bonds of S atom with other neighbouring atoms (As, for example) create a bond angle of about  $100^\circ$  [8,19], it can be easily shown that almost 70% of the drawing sphere is the bond-free solid angle. The real value of this volume can be somewhat reduced, accepting that lone-pair lp-charge density is additionally distributed in this space. Since the typical single vacancy volume in ChG is as high as  $25\text{-}30 \text{ \AA}^3$  [8], the maximum value of an associated free volume around each normally-coordinated chalcogen atom is  $\sim 15 \text{ \AA}^3$ .

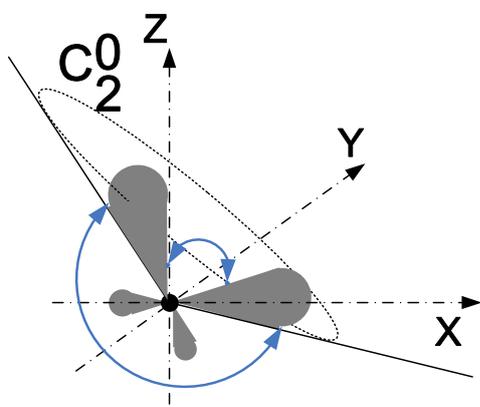


Fig. 1. Local bond-charge density distribution around sulphur  $S_2^0$  atom within normally-coordinated covalent-bonded ChG network.

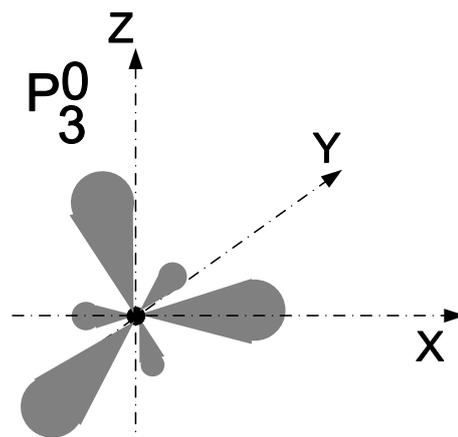


Fig. 2. Local bond-charge density distribution around arsenic  $As_3^0$  atom within normally-coordinated covalent-bonded ChG network.

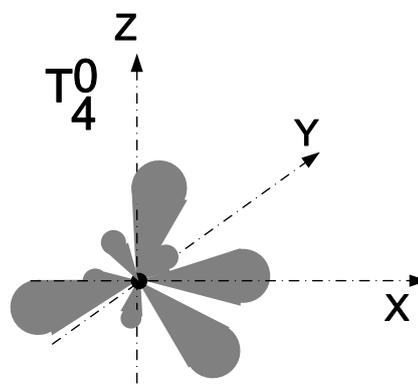


Fig. 3. Local bond-charge density distribution around germanium  $Ge_4^0$  atom within normally-coordinated covalent-bonded ChG network.

These nanovoids are introduced into structural network along with each chalcogen atom whichever the network nature (crystalline or amorphous).

The similar consideration shows that in group-V elements (pnictogens), which are three-fold coordinated, these nanovoids are smaller with a character volumes of  $\sim 10 \text{ \AA}^3$  [10,19]. Within this estimation, it is accepted that all three covalent chemical bonds around pnictogen atoms are located only in one half of a coordination sphere [19]. At the same time, the four-fold coordinated Ge atom with  $sp^3$ -hybridised covalent bonding has no accompanied free-volume nanovoids [19].

By putting within this concept that bond charge cone is distributed uniformly between existing "dumb-bells" of covalent bonds (see Fig. 1,2,3), it can be estimated that free-volume additives caused by one-bond lack reaches  $\sim 14\%$  from overall free volume for  $S_1^-$  (Fig. 4),  $\sim 17\%$  for  $As_2^-$  (Fig. 5) and  $\sim 25\%$  for  $Ge_3^-$  extended defects (Fig. 6). Therefore, the overall free volume per one negatively-charged defect will be  $43 \text{ \AA}^3$  for  $S_1^-$  surrounded by As atom,  $33 \text{ \AA}^3$  for  $As_2^-$  surrounded by two S atoms and only  $12 \text{ \AA}^3$  for  $Ge_3^-$  surrounded by three S atoms.

Thereby, within this approach, we can treat the studied extended defects as structural anomalies in ChG having three types of irregularities:

- the wrong number of neighbouring directly covalent-bonded atoms (over- or under-coordinated) in respect to non-defect glass-forming backbone normally coordinated due to  $8-N$  rule [8,9],
- the excess of uncompensated local electrical charge (negative in case of under-coordination or positive in case of over-coordination),
- the accompanied free volume due to lack of one covalent chemical bond in the vicinity of negatively-charged under-coordinated atom (see Fig. 4-6).

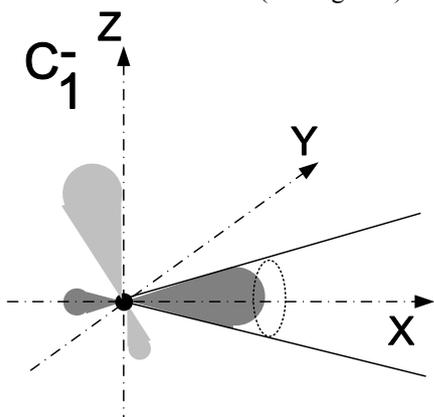


Fig. 4. Extended defect in ChG based on negatively-charged under-coordinated chalcogen atom  $C_1^-$  (the accompanied free volume due to lack of one covalent bond is light-distinguished).

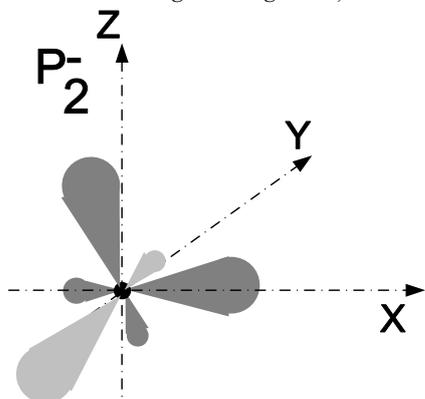


Fig. 5. Extended defect in ChG based on negatively-charged under-coordinated chalcogen atom  $P_2^-$  (the accompanied free volume due to lack of one covalent bond is light-distinguished).

Two latter features occur noticeable effect on PALS data because of expected significant changes in the positron-trapping modes of ChG due to local electrical charge (negative) and free volume excess. In strong respect to the above consideration, we can assume that input of  $S_1^-$  extended defects having the greatest free volume will be the most essential into defect-related PALS channel in ChG, while only negligible under-margin effect is expected to be for  $Ge_3^-$  defects surrounded by three S atoms. Within covalent bond lengths balance in the studied

As(Sb)-Ge-S systems in respect to [8] (2.28 Å for S-As, 2.24 Å for S-Ge and 2.20 Å for S-S), we can estimate that the appeared  $S_1^-$ -related free volume is  $32 \text{ \AA}^3$  for sulphur surrounding,  $43 \text{ \AA}^3$  for arsenic surrounding and  $41 \text{ \AA}^3$  for germanium surrounding. In case of  $As_2^-$  defect in sulphur surrounding, this free volume is at the level of  $33 \text{ \AA}^3$ , while only  $12 \text{ \AA}^3$  in case of  $Ge_3^-$  defect in the same sulphur surrounding.

Therefore, it should be noted that only  $S_1^-$  extended defects change significantly the measured PALS data, while  $As_2^-$  defects show only slight influence and  $Ge_3^-$  defects occur rather under-margin influence. This conclusion correlates well with experimental PALS results presented in Table 2.

Indeed, in case of Ge-As-S ChG, the appeared radiation-induced defects are of all types ( $S_1^-$ ,  $As_2^-$  and  $Ge_3^-$ ) [1,5]. This follows from high energetic barriers proper to both As-S and Ge-S glass-forming sub-systems [8]. Because of large associated free volume mainly for negatively-charged  $S_1^-$  and  $As_2^-$  defects (even in a case of their relatively small concentration near 5-7 % [1,4,5]), these radiation-structural transformations significantly modify measured PALS data. As a result, the positron trapping saturates in these defects giving a well-distinguished long-lived PALS component with  $\tau_2$  close to 0.39 ns in irradiated ChG (see Table 2).

In contrast, within Ge-Sb-S system, only negatively-charged  $Ge_3^-$  defects dominate in the irradiated samples, since Sb-related defects are supposed to be unstable because of low energetic barrier of backward defect-annihilated dissociation in Sb-S sub-system [8]. But these  $Ge_3^-$  defects have too small associated free volume (near  $12 \text{ \AA}^3$ ) to be detectable by PALS technique. As a result, there were no any significant changes in the measured PALS data (compare Table 1 and 2). This result well correlates with recent study of  $\gamma$ -induced structural transformations in glassy Ge-Sb-S using high-resolution X-ray photoelectron spectroscopy, showing only  $Ge_3^-$  defects in the structure of  $\gamma$ -irradiated samples [20].

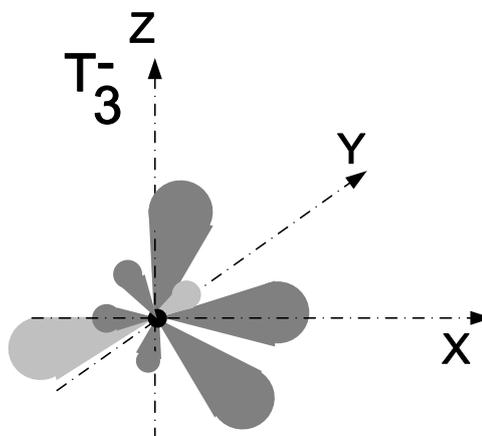


Fig. 6. Extended defect in ChG based on negatively-charged under-coordinated chalcogen atom  $T_3^-$  (the accompanied free volume due to lack of one covalent bond is light-distinguished).

The greater ( $\tau_2 - \tau_b$ ) differences (close to 1.3 ns) and  $\tau_2/\tau_b$  ratio (close to 1.6-1.7) in Ge-Sb-S ChG can be well explained as character values proper to native positron-trapping extended defects. These non-defect free volumes appear in Ge-based ChG owing to geometrical specifics in their structure with interlinked corner- and edge-sharing tetrahedra [8].

It should be noted that, being strongly within two-state positron trapping model [14], the average positron lifetime  $\tau_{av}$  increases after  $\gamma$ -irradiation in As-Ge-S ChG testifying in a favour of  $S_1^-$  defects preference. However, if different deconvolution procedures are explored (one-component saturated positron trapping in non-irradiated state and two-component positron trapping in after-irradiated state), the observed tendency attains opposite character. This is probably caused by different measurement statistics used for irradiated and non-irradiated ChG samples as it noted in [21]. To compare correctly defect-related positron trapping modes in the studied ChG, the same mathematical deconvolution route should be applied whichever the glass composition and irradiation conditions. In contrast, the two-component deconvoluted PALS trapping modes of Ge-Sb-S ChG show no significant radiation-induced changes in full respect to PALS-insensitive  $Ge_3^-$  defects preference.

#### 4 Conclusion

Radiation-induced extended defects in ChG within ternary Ge-As-S and Ge-Sb-S systems can be identified using PALS technique, provided associated free-volume nanovoids are large enough to modify the measured PALS data. This condition satisfies well for Ge-As-S ChG with under-coordinated  $S_1^-$  and  $As_2^-$  coordination defects. In contrast, there are no significant free-volume-based extended defects in Ge-Sb-S ChG, showing only negligible irradiation effect on PALS data.

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