Free-Volume Nanostructurization in Ga-Modified As$_2$Se$_3$ Glass

Ya. Shpotyuk$^{1,2,3,*}$, A. Ingram$^4$, O. Shpotyuk$^{5,6}$, A. Dziedzic$^2$, C. Boussard-Pledel$^3$ and B. Bureau$^3$

**Abstract**

Different stages of intrinsic nanostructurization related to evolution of free-volume voids, including phase separation, crystalline nuclei precipitation, and growth, were studied in glassy As$_2$Se$_3$ doped with Ga up to 5 at.%, using complementary techniques of positron annihilation lifetime spectroscopy, X-ray powder diffraction, and scanning electron microscopy with energy-dispersive X-ray analysis. Positron lifetime spectra reconstructed in terms of a two-state trapping model testified in favor of a native void structure of g-As$_2$Se$_3$ modified by Ga additions. Under small Ga content (below 3 at.%), the positron trapping in glassy alloys was dominated by voids associated with bond-free solid angles of bridging As$_{2/3}$Se$_{4/2}$ units. This void agglomeration trend was changed on fragmentation with further Ga doping due to crystalline Ga$_2$Se$_3$ nuclei precipitation and growth, these changes being activated by employing free volume from just attached As-rich glassy matrix with higher content of As$_{2/3}$Se$_{4/2}$ clusters. Respectively, the positron trapping on free-volume voids related to pyramidal AsSe$_{3/2}$ units (like in parent As$_2$Se$_3$ glass) was in obvious preference in such glassy crystalline alloys.

**Keywords:** Chalcogenides, Nanostructurization, Phase separation, Crystallization, Positron annihilation lifetime spectroscopy

**Background**

Ga-modified chalcogenide glasses (ChG) are known to be of high importance in view of their perspectives for modern IR photonics as active media with improved optical functionality, revealed, in part, when these glasses are doped with rare earth (RE) activators such as Pr$^{3+}$, Dy$^{3+}$, Tb$^{3+}$, Er$^{3+}$, and Nd$^{3+}$ [1–9]. Such ChG demonstrates an obvious tendency to nanostructurization by forming intrinsic inhomogeneities because of strong Ga affinity to chemical interaction with chalcogens, this process being governed by Ga content and preferential type of its environment in parent glass matrix [4, 10–16]. In dependence on these pre-requisites, extra Ga additions can result in phase separation, nucleation and, finally, crystal growth, leading to stabilization of different crystalline Ga$_2$Se$_3$ polymorphs. Thus, under small Ga content (2–3 at.%) added in mixed Se–Te environment of TAS-235 glass (e.g., glassy g-As$_{80}$Se$_{50}$Te$_{20}$ alloy), the nanoscale droplets of dominated y-Ga$_2$Se$_3$ phase (a few hundreds of nanometers in sizes) can be displayed, while at more enhanced Ga content reaching 5–10 at.%, this process extends over a microscale, when these crystallites grow to a few micrometers in sizes [8, 13]. In contrast, in Se-rich environment of Ge-based GeSe$_2$–Ga$_2$Se$_3$ glass at heat treatment not too far above $T_g$ these Ga additions provoke formation of some multication crystallites like GeGa$_4$Se$_8$ [14–16] or Ga$_2$Ge$_5$Se$_8$ [12]. Crystallite growth and stabilization in ChG matrices is accompanied by complicated changes stretching over both atomistic (atomic-specific) and void (atomic-deficient) structural levels. The latter is related to the evolution of some free-volume entities (typically sub-nanoscale voids, vacancies, vacancy-like clusters, etc.), when inner holes are agglomerated to form spaces of reduced electron density available for orientation stabilization of growing crystallites or, conversely, these holes are fragmented on smaller parts ensuring energetically favorable localization for growing crystallites in a predominantly glass environment [13]. In case of technologically controlled crystallization, it is possible to manufacture an important class of glass ceramics transparent in IR region, which possess much better mechanical reliability than their glassy counterparts [17]. But in most cases, these crystallization processes are
undesirable, especially when ChG should be doped with RE ions to get tunable, high-power, secondary remote mid-IR sources [9], or drawn into fiber to produce active media for optical biosensing [18].

In this work, the physical peculiarities of Ga-affected nanostructurization associated with subsequent stages of glass structure modification (phase separation, nucleation, and crystallization), overall described at atomic-deficient void level, are comprehensively studied in g-As$_2$Se$_3$, one of the well-known canonical representatives of functional chalcogenide photonics [19].

**Methods**
The studied samples of Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100-x}$ (x = 0, 1, 2, 3, 4, 5) alloys were prepared from high-purity elemental constituents (5 N or more) by conventional melt-quenching technique as described elsewhere [9, 11]. Total weight of ingredients inserted in silica ampoules of 10 mm in diameter used for melting was 30 g. The ampoule was sealed under a vacuum and heated at 900 °C in a rocking furnace for 10 h, followed by quenching into room temperature water at 700 °C. Then, these alloys were annealed during 5 h at 10 K below glass transition to remove mechanical strains that appeared during quenching, cut into disks of ~2 mm in thickness, and finally, polished to high optical quality.

The crystalline state of the samples was controlled with X-ray powder diffraction (XRPD), experimental data being collected in the transmission mode on a STOE STADI P diffractometer (Cu Kα$_1$-radiation). The crystal structures of phases were refined by the Rietveld method with the program FullProf2k (v. 5.40) [20]. The surface morphology of fresh cut sections of the prepared alloys was tested using scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) analyzer FEI QUANTA 3D 200i (Hillsboro, OR, USA).

Positron annihilation lifetime (PAL) spectra were registered using fast coincidence system ORTEC of 230 ps resolution (the full width at half maximum) operated at high-stabilized normal measuring conditions. The pair of identical plane-parallel samples of each composition in sandwich geometry was employed for the measurements. The source contribution from $^{22}$Na isotope of low activity was taken at the level of 12 % (r = 0.372 ns). To ensure reliable PAL data, three independent measuring cycles (with near 1 M elementary positron annihilation events) were performed. Experimental results were fitted by two single exponents under normalized intensities ($I_1 + I_2 = 1$) using LT 9.0 program [21], the corresponding accuracies in lifetimes $\tau_1$ and intensities $I_1$ being not worse ±0.005 ns and 0.5 %, respectively. Mathematical formalism of the known two-state positron trapping model with only one kind of traps [22–26] was utilized to parameterize mean $\tau_{av}$ and defect-free bulk $\tau_0$ lifetimes, as well as trapping rate in defects $\kappa_d$. In addition, the difference between defect-related $\tau_d = \tau_3$ and bulk positron lifetimes ($\tau_d - \tau_0$) was taken as a signature of size of positron traps in terms of equivalent number of vacancies, and $\tau_d/\tau_0$ ratio was ascribed to nature of these defects [22]. The fraction of trapped positrons $\eta = \tau_1/\kappa_d$ was also controlled in this research.

**Results and Discussion**
Different stages of intrinsic nanostructurization can be activated in g-As$_2$Se$_3$ in dependence on the amount of added Ga [9, 11]. Firstly, at small enough Ga content within studied Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100-x}$ cut section not exceeding 3 at. %, the melt-quenched alloys are fully in a glassy state, since no any sharp reflexes (but only wide-stretched halos typical for amorphous substances) are detected on the XRPD patterns [9]. Further, at higher Ga content, some crystallities of low-temperature α-Ga$_2$Se$_3$ phase appear in glassy crystalline g/c-Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{95}$ alloy, the crystallized phase being well identified due to six sharp XRPD peaks corresponding to one of cubic Ga$_2$Se$_3$ polymorphs with a space group of F43m (JCPDS ICDD card no. 89-7201) [9, 27–29]. The most pronounced crystallization effect is revealed in g/c- Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{95}$, where ten separate XRPD peaks centered near 28.5°, 33°, 47°, 56°, 69°, 76°, 87.5°, 94.5°, 106°, and 113° 2θ are detected (Fig. 1). These peaks can be well indexed assuming fcc Ga$_2$Se$_3$ structure of zinc blende type (F43m space group), which allow to estimate the unit cell lattice parameter $a = 5.4576(6)$ Å (with respective unit cell volume $V = 162.55(3)$ Å$^3$). In accord with similar behavior in Ga-doped g-As$_{30}$Se$_{50}$Te$_{20}$ [8, 13], this effect can be ascribed to preferential formation of high-temperature γ-Ga$_2$Se$_3$ phase.

Under this Ga content, the crystallization is most evident, the cones of four to six separate Ga$_2$Se$_3$ crystallites.

![Fig. 1](image-url) Experimental XRPD pattern of g/c-Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{95}$ sample (blue color) in comparison with theoretical diffraction pattern of Ga$_2$Se$_3$ high-temperature phase of ZnS structural type. (red color, hkl indexes are indicated above the peaks)
(each less than 1 μm) being well distinguished at cut surface of g/c-Ga\textsubscript{5}(As\textsubscript{0.4}Se\textsubscript{0.6})\textsubscript{95} alloys (Fig. 2). The chemical composition of the sample was checked in two different spots, these being uniform surface area without visible inclusions (A) and one with some agglomerated crystallites (B). The corresponding EDS spectra from these spots detected up to 15 keV (current 0.65 nA) are shown in Fig. 3. Only arsenic As, selenium Se, and gallium Ga were defined as main elements responsible for the observed peaks on these spectra, located respectively to their L\textalpha{} and K\textalpha{} states. Despite uncertainties due to large scatter in the experimental points, a sharp increase in Ga and decrease in As content was detected from a crystallite-covered area. In opposite, the uniform sample matrix near crystallites was enriched on As and deficient on Ga, while Se content was nearly the same over a whole sample’s surface. These results testify that extraction of Ga\textsubscript{2}Se\textsubscript{3} phase is indeed the most plausible reason for growing crystallites.

The above processes essentially modify atomic-deficient void structure of Ga\textsubscript{x}(As\textsubscript{0.4}Se\textsubscript{0.6})\textsubscript{100-x} alloys, as it follows from PAL spectra reconstructed within the two-component fitting procedure (Fig. 4) and best-fit positron trapping parameters gathered in Table 1. Since neither average \(\tau_{av}\) nor defect-free bulk \(\tau_{b}\) positron lifetimes are changed under Ga additions, the two-state trapping model based on one preferential type of positron traps [22–26] can be validated as most relevant to the physically realistic channel of positron...
annihilation in these alloys. The volumes of these traps (e.g., sizes of low-electron density spaces) in g or g/c alloys are reflected by defect-related $\tau_2$ lifetimes, while their contents being proportional to intensities of the second fitting components ($I_2$) [22]. Thus, the positron trapping modes correspondingly recalculated in respect to the above fitting parameters, including trapping rate in defects $\kappa_d$ ($\tau_2-\tau_b$) difference, $\tau_2/\tau_b$ ratio, and fraction of trapped positrons $\eta$, can be ascribed to the same type of traps as those characteristic for g-As$_2$Se$_3$ [23, 30–33], which are subjected to Ga-activated compositional modification within the Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100-x}$ system.

In g-As$_2$Se$_3$, the positron trapping is defined by spatial distribution of low-electron density spaces (native free-volume voids) formed within cycle-type formations of chalcogen-interlinked polyhedrons, such as AsSe$_{3/2}$ pyramids (the fractional subscript means atoms simultaneously belonging to two neighboring units) [23, 31].

Deviation in the number of elements forming such cycle-type formations in a glass, they can be considered as network remainders of strict 12-membered cycles in a crystalline structure of rhombohedral As$_2$Se$_3$ [34]. In void structure evolution in ChG, an essential role belongs to spaces in the nearest atomic surrounding, which are free of electron density due to directionality of covalent bonds, e.g., bond-free solid angles (BFSA) in terms of Kastner [35]. Depending on electronegativity of neighbors [36], these intrinsic local spaces can be associated with effective neutral (Se atoms in –Se–Se–Se– chain- and ring-like fragments), positive (As atoms in the top of AsSe$_{3/2}$ pyramids), or negative (Se atoms within heteronuclear =As–Se–As= bridges, e.g., in the bottom of neighboring AsSe$_{3/2}$ pyramids) electrical charge [23, 31, 37]. So the most efficient positron traps in a covalent-bonded network of g-As$_2$Se$_3$ represent geometrical free-volume spaces within corresponding cycle-type formations of interlinked

![Fig. 4 Raw PAL spectrum of crystallized Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100-x}$ alloy reconstructed from a two-component fitting at the general background of source contribution (bottom inset shows statistical scatter of variance)](image)

**Table 1** Fitting parameters and positron trapping modes describing two-component reconstructed PAL spectra of Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100-x}$ alloys

| Sample, state | Fitting parameters | Positron trapping modes |
|---------------|--------------------|-------------------------|
|               | $\tau_1$, ns       | $\tau_2$, ns            | $I_2$, a.u. | $\tau_{av}$, ns | $\tau_b$, ns | $\kappa_d$, ns$^{-1}$ | $\tau_2-\tau_b$, ns | $\tau_2/\tau_b$, – | $\eta$, – |
| g-As$_2$Se$_3$ | 0.210              | 0.360                   | 0.462      | 0.279           | 0.260           | 0.92            | 0.10                 | 1.39            | 0.19            |
| g-Ga$_1$(As$_{0.4}$Se$_{0.6}$)$_{99}$ | 0.216              | 0.371                   | 0.408      | 0.279           | 0.261           | 0.78            | 0.11                 | 1.42            | 0.17            |
| g-Ga$_2$(As$_{0.4}$Se$_{0.6}$)$_{98}$ | 0.223              | 0.382                   | 0.401      | 0.287           | 0.267           | 0.75            | 0.11                 | 1.43            | 0.17            |
| g-Ga$_3$(As$_{0.4}$Se$_{0.6}$)$_{97}$ | 0.211              | 0.365                   | 0.457      | 0.281           | 0.261           | 0.91            | 0.10                 | 1.39            | 0.19            |
| g/c-Ga$_4$(As$_{0.4}$Se$_{0.6}$)$_{96}$ | 0.204              | 0.359                   | 0.488      | 0.280           | 0.258           | 1.03            | 0.10                 | 1.39            | 0.21            |
| g/c-Ga$_5$(As$_{0.4}$Se$_{0.6}$)$_{95}$ | 0.207              | 0.362                   | 0.462      | 0.279           | 0.258           | 0.95            | 0.10                 | 1.40            | 0.20            |
AsSe$_{3/2}$ pyramids (atomic-accessible void core) surrounded by low-electron density spaces originated from atomic environment due to strict directionality of covalent chemical bonds (atomic-inaccessible void shell). The possible configurations of some void shells (e.g., BFSA) in ChG systems are considered in more detail elsewhere [23, 37, 38]. If only geometrical free volumes (void cores) have been decisive in a positron trapping in ChG, then defect-related positron lifetime $\tau_2$ would be in strong correlation with molar volume in a g-As–Se system. However, an obviously opposite tendency is observed in g-As–Se, e.g., increase in $\tau_2$ positron lifetime with going from looser Se-rich towards stoichiometric As$_2$Se$_3$ and As-rich glasses [31], thus meaning an importance of contribution from agglomerated BFSA (void shells) surrounding geometrical voids. From a standpoint of positron trapping [22], the heteroatomic environment around a chalcogen atom has an obvious preference. Indeed, because of difference in the electronegativity [36], such low-electron density sites carry an effective negative charge, thus transforming corresponding free-volume void in a prototype of cation vacancy in a crystal. This local electrical charge distribution is not characteristic of pure homoatomic Se chains or rings, resulting in reduced positron trapping in Se-rich ChG [31, 32].

In the network of Se-interlinked AsSe$_{3/2}$ pyramids forming the structure of g-As$_2$Se$_3$, two of three Se atoms in the bottom of the AsSe$_{3/2}$ pyramid contribute with their BFSA towards free-volume void, while the third Se atom contradicts this because of electron density cone of a covalent bond directed in an opposite hemisphere as void. The geometrically optimized configuration of such AsSe$_{3/2}$ pyramid cluster computed with ab initio quantum chemical modeling [39] is shown in Fig. 5. Thus, the most expected positron traps in g-As$_2$Se$_3$ can be imagined as free-volume voids surrounded by neighboring BFSA originated from two Se atoms (in heteroatomic =As–Se–As= environment) of the AsSe$_{3/2}$ pyramid. The expected volumes of such positron traps (near ~90 Å$^3$) can be simply estimated from corresponding defect-related positron lifetime $\tau_2 \cong 0.36$ ns in respect to Jensen’s calculations [33].

Possible configuration of such void in orpiment As$_2$S$_3$ crystal, the known crystalline counterpart of As$_2$Se$_3$ [34], reproduced in respect to electronic structure calculations for mineral arsenic sulfide As$_2$S$_3$ performed using Exciting package [40] is depicted in Fig. 6. Undoubtedly, such voids remain in melt-quenched state, thus defining preferential positron trapping in ChG, while voids surrounded by As-based BFSA are rather ineffective for trapping because of repulsive potential for positrons [31, 32]. With transition to over-stoichiometric As-rich ChG, the bridging As$_2$Se$_{4/2}$ units based on homopolar As–As bonds appear in a network of AsSe$_{3/2}$ pyramids. Both pairs of Se atoms at the edges of the As–As bond contribute fully to free-volume void, since their BFSA are directed to one hemisphere without any restrictions on opposite directionality of Se atoms like in AsSe$_{3/2}$ units (see Fig. 5). So the volumes of such voids grow (in full harmony with decreased atomic densities [34]), thus resulting in enhanced defect-related $\tau_2$ lifetimes for ChG consisting of these structural units, while their concentration (reflected in $I_2$ intensity) essentially drops in view of chemical formulation [23, 41].

This effect is dominated in g-As$_2$Se$_3$ at small Ga addition, specifically in g-Ga$_{1-x}$As$_{2x}$Se$_3$$_{0.98}$ and g-Ga$_{2}$As$_{0.5}$Se$_{0.5}$$_{0.98}$, where increase in $\tau_2$ lifetime from 0.360 to 0.382 ns (Table 1) is caused by transition to positron trapping on free-volume voids neighboring with Se-type BFSA of As$_2$Se$_{4/2}$ units. The bridging As$_2$Se$_{4/2}$ clusters appear due to deficit in Se environment for As atoms because of Ga doping at small concentration. Indeed, chemical interaction in a Ga–As–Se system is governed by Ga bonding. By accepting energies for homonuclear Ga–Ga, As–As, and Se–Se bonds as 34.1, 32.1, and 44.0 kcal/mol, respectively [36, 42], the energies for heteronuclear Ga–Se, Ga–As, and As–Se bonds can be estimated in respect to known Pauling’s formula [36] as 55.2, 37.2, and 41.7 kcal/mol, respectively. Thereby, the Ga dopants form polyhedra with Se atoms inserted in remainder of the As–Se
Another g-Ga\(_2\)(As\(_{0.4}\)Se\(_{0.6}\)) alloy, possessing positron trapping modes which are rather close to the ones of g-As\(_2\)Se\(_3\) (Table 1), is obviously exceptional from the above correlation line. Defect-related annihilation channel in this ChG is presumably disturbed due to crystalline nuclei precipitation of separated Ga\(_2\)Se\(_3\) phase, like it occurred in 80GeSe\(_2\)-20Ga\(_2\)Se\(_3\) glass under thermally induced “cold” crystallization [16]. At this stage, the Ga\(_2\)Se\(_3\) crystallites do not grow enough to be detected quite reliably with XRPD. The nuclei precipitation process is activated by employing free volume of just attached As-rich matrix with preferential content of bridging As\(_2\)Se\(_{4/2}\) clusters. Correspondingly, the defect-related \(\tau_2\) lifetime drops down to the value of \(\sim 0.36\) ns, which is characteristic of positron trapping on free-volume voids within As\(_2\)Se\(_{4/2}\)-based cycle formations in stoichiometric g-As\(_2\)Se\(_3\) (see Table 1).

Conclusions

The nanostructurization processes related to evolution of free-volume voids were studied in glassy As\(_2\)Se\(_3\) affected by different amounts of Ga additions (up to 5 at. %), using positron annihilation lifetime spectroscopy, the lifetime spectra being analyzed within a canonical two-component model with one preferential type of positron traps. It was shown that below 3 at. % of Ga, when glass formation was not essentially violated, the positron trapping is dominated on intrinsic voids associated with bond-free solid angles of bridging As\(_2\)Se\(_{4/2}\) units, thus producing an increase in defect-related lifetime from 0.360 to 0.382 ns at the cost of reduced second-component intensity and positron trapping rate in defects. This void agglomeration trend was changed on opposite (void fragmentation) at greater Ga content in As\(_2\)Se\(_3\) glass due to crystalline Ga\(_2\)Se\(_3\) nuclei precipitation and growth. The observed crystallization processes were activated by employing free volume of just attached As-rich matrix with higher content of As\(_2\)Se\(_{4/2}\) clusters. In such glassy crystalline alloys, the positron trapping on free-volume entities related to pyramidal As\(_2\)Se\(_{3/2}\) units (as in parent As\(_2\)Se\(_3\) glass) was in obvious preference, tending overall annihilation-like void fragmentation without notable changes in sizes of positron traps.

Abbreviations

BFSA: bond-free solid angle; ChG: chalcogenide glass; EDS: energy-dispersive spectroscopy; PAL: positron annihilation lifetime; RE: rare earth; SEM: scanning electron microscope; XRPD: X-ray powder diffraction.

Competing Interests

The authors declare that they have no competing interests.

Authors’ Contributions

All authors (YaSh, Al, OSh, AD, CB, BB) developed the methodological algorithms to treat experimental PAL spectra. Al and YaSh performed the experiments to characterize the samples. YaSh, CB, and BB prepared the tested objects. AD and ShYa performed the SEM and EDS analyses. All authors read and approved the final manuscript.

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Author details

1Department of Electronics, Ivan Franko National University of Lviv, 107, Tarnavskogo str., 79017 Lviv, Ukraine. 2Centre for Innovation and Transfer of Natural Sciences and Engineering Knowledge, University of Rzeszow, 1, Pigionia str., 35-959 Rzeszow, Poland. 3Laboratoire Verres et Céramiques, UMR-CNRS 6226, Université de Rennes 1, 35042 Rennes, Cedex, France.
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