

Nanoscale mechanism of rare-earth doping in Ga-codoped glassy As-Sb selenides

Yaroslav Shpotyuk

► **To cite this version:**

Yaroslav Shpotyuk. Nanoscale mechanism of rare-earth doping in Ga-codoped glassy As-Sb selenides. Journal of the American Ceramic Society, Wiley, 2017, 100 (9), pp.3865-3874. 10.1111/jace.14909. hal-01614772

HAL Id: hal-01614772

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01614772>

Submitted on 16 May 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DR. YA. SHPOTYUK (Orcid ID : 0000-0001-6710-7839)

Article type : Article

Editor: Prof. Pierre Lucas

Nanoscale mechanism of rare-earth doping in Ga-codoped glassy As-Sb selenides

Yaroslav Shpotyuk^{1-3,*}

¹*Centre for Innovation and Transfer of Natural Sciences and Engineering Knowledge, Faculty of Mathematics and Natural Sciences, University of Rzeszow, 1, Pigoia str., 35-959 Rzeszow, Poland*

²*Department of Sensor and Semiconductor Electronics, Ivan Franko National University of Lviv,*

107, Tarnavskogo str., 79017, Lviv, Ukraine

³*Laboratoire Verres et Céramiques, UMR-CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France*

**The corresponding author e-mail: yashpotyuk@gmail.com*

Abstract

The method of annihilating positrons in positron annihilation lifetime measuring mode is applied to study mechanism of rare-earth doping in Ga-codoped arsenic selenide As_2Se_3 glass modified with Sb. The atomic-deficient structure of parent As_2Se_3 glass is imagined as containing positron trapping sites in the form of free-volume voids within cycle-type arrangement of corner-sharing trigonal $\text{AsSe}_{3/2}$ pyramids, composed of atomic-accessible geometrical holes arrested by surrounding atomic-inaccessible Se-based bond-free solid angles. The Ga-codoping in As_2Se_3 glass causes gradual decrease in trapping rate and fraction of trapped positrons due to agglomeration of free-volume voids. Partial As-to-Sb replacement in Ga-codoped As-Se glasses leads to better stability against crystallization processes and

possibility to further rare-earth doping without principal changes in the type of positron trapping defects. Effect of 500 wppm of Pr^{3+} in $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ glass is explained in terms of competitive contribution of changed occupancy sites in Ga-modified glassy network available for rare-earth ions and annihilating positrons.

Keywords: nanoscale, rare-earth ions, chalcogenide glasses; nanoinhomogeneities, positrons.

I. Introduction

Rare-earth (RE) doped chalcogenide glasses (ChG) attract great attention in modern materials science community as versatile device media for a variety of active applications in mid-IR optics including fiber-optics amplifiers and IR lasers.^{1,2,3} However, this sphere of *chalcogenide photonics* has still being highly disputable now because of insufficient knowledge on the nature of RE-activated functionality in covalent-saturated ChG networks.

To be functioning, the RE atoms should occupy an electrically active “+3” state, which is principally impossible for typical ChG matrices under a condition of *global electroneutrality* proper to full saturation of covalent bonding in respect to the known Mott’s $8-N$ rule.^{4,5} Local structural nanoinhomogeneities possessing an effective negative electrical charge are crucially desirable to compensate positive electrical charge of RE ions embedded in covalent-linked glassy skeleton. This problem can be resolved extrinsically due to some chemical modifiers such as Ga or In added to ChG in small amounts, which don’t disturb their glass-forming ability.⁶⁻¹⁰ Preliminary ChG doping with these elements (which therefore can be conditionally defined as Ga- or In-*codoping*) seems most efficient way to stabilize randomly-distributed sites in ChG matrix possessing local excess of uncompensated negative electrical

charge along with unoccupied atomic-accessible space (named as free-volume holes) needed to reside the electrically-active RE dopants without any clustering.

With this in mind, the present problem of RE-activated ChG functionality could be reexamined at a nanoscale as returning to known *filling-space controversy* in a *host-guest* chemistry.^{11,12} Successful RE-doping is relied on such *nanospace-tailoring* technology, when some rigid chemical bonding arrangement is destructed in a *host* glassy network at a preliminary stage of Ga/In-codoping to create appropriate sites available for occupation by *guest* RE ions at a further stage of RE-doping.

In this work, the method of annihilating positrons in positron annihilation lifetime (PAL) measuring mode, which is known to be advanced instrumentation tool efficiently exploring nanospace at atomistic and sub-atomistic length-scales,¹³⁻¹⁸ will be applied to study the mechanism of RE-doping (by Pr^{3+} ions) in Ga-codoped arsenic-antimony selenide $(\text{As/Sb})_2\text{Se}_3$ ChG.

II. Experimental

(1) ChG preparation and input characterization

In this work, the ChG probes within $\text{Ga}_x[(\text{As/Sb})_{0.40}\text{Se}_{0.60}]_{100-x}$ cut-section will be examined in a row of subsequent steps from (1) stoichiometric glassy arsenic selenide $\text{g-As}_2\text{Se}_3$, serving as starting point, then to (2) Ga-codoped $\text{g-As}_2\text{Se}_3$ of optimal $\text{g-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$ composition, further to (3) optimal Ga-codoped As-Sb selenide $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$, and finally to (4) $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} .

These ChG were prepared from high-purity elemental precursors, e.g. Ga (7N), As (5N), Se (5N), and Pr_2Se_3 (3N), the ingredients being specially purified by distillation with low

evaporation rate to remove impurities (O, C, H₂O, and SiO₂). Appropriate amounts of ingredients with total weight close to 30 g were put into silica tube of 10 mm diameter. Then, the ampoules were sealed under a vacuum, heated up to 900 °C with 2 °C/min rate and stayed at this temperature for 10 h in a rocking furnace with further quenching into water from 700 °C. To remove mechanical strains appeared during rapid quenching, the alloys were annealed during 6 h at temperature of 10 °C less than glass transition. Then, the obtained rods were cut into ~2mm disks and polished. A more detailed description of the ChG preparation procedure can find elsewhere.¹⁹⁻²¹

With respect to eventual using of RE-doped ChG in fiber optics,^{1,2} the thermal behavior of each sample was examined using differential scanning calorimetry (DSC) with TA Instruments Q20 (TA Instruments, Inc., New Castle, DE, USA). Typically, 10 mg bulk samples were sealed in standard aluminum pans and heated at 10 °C/min heating rate. The glass transition (T_g) and crystallization (T_x) temperatures were taken as onset points at the endothermic heat flow peaks with a resulting accuracy no worse than ± 2 °C. To be suitable candidate for fiber drawing, the ChG should be stable against crystallization. The stability of ChG on reheating above T_g can be estimated by the Hruby parameter determined as $\Delta T=(T_x-T_g)$ difference also known as glass stability factor.²² Typically, this ΔT value should be higher than 100 °C, which is assumed to be sufficient for successful fiber drawing.

The X-ray diffractometer PANalytical X'Pert Pro (Cu K α radiation, $\lambda=1.5418$ Å) was used to check an amorphous nature of the prepared alloys. The X-ray diffraction (XRD) patterns of bulk ChG samples were collected in reflection mode at room temperature in the 2θ range from 5 to 90°.

The densities ρ of polished disk samples were measured using the Archimedes displacement method with *Mettler Toledo* analytical balances operated at room temperature

using ethanol. The mean value of three tests was taken for each sample as final density ρ , the accuracy being $\pm 0.005 \text{ g}\cdot\text{cm}^{-3}$. The molar volumes V_m of the ChG samples were calculated at the basis of measured densities ρ as:

$$V_m = \frac{\sum_{i=1}^N x_i M_i}{\rho}, \quad (1)$$

where M_i and x_i were the molar weight and percentage of each element in the compound, respectively.

(2) Optical characterization

The optical transmission spectra of the samples in the range of 0.8-2.5 μm were registered using UV/Vis/NIR spectrophotometer PerkinElmer LAMBDA 950 operating with 2 nm resolution, while IR transmission spectra in the range of 1.5-25 μm were measured using Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. The fluorescence emission in the range of 850-1400 nm was recorded using Fluorolog-3 (Horiba) spectrometer equipped with PMT detector. The 450 W Xenon lamp eliminating in 500-800 nm range was used for excitation, and special cuvette was employed to perform low-temperature fluorescence measurements under liquid nitrogen (77 K).

(3) Positron annihilation studies

The PAL spectroscopy was employed first to trace the evolution of atomic-deficient free-volume structure of As_2Se_3 -based ChG, affected in subsequent steps of Ga-codoping and RE-doping.

The PAL measurements were performed using a fast-fast coincidence system of 230 ps resolution based on two Photonis XP2020/Q photomultiplier tubes coupled to BaF₂ scintillator 25.4A10/2M-Q-BaF-X-N detectors (Scionix, Bunnik, Holland) and ORTEC[®] electronics (ORTEC, Oak Ridge, TN, USA). The reliable PAL spectra were detected in a normal-measurement statistics (~1 M coincidences) under stabilized temperature (22 °C) and relative humidity (35%). The channel width of 6.15 ps allows a total number of channels to be 8000. The radioactive ²²Na isotope of relatively low ~50 kBq activity prepared from aqueous solution of ²²NaCl wrapped by Kapton[®] foil (DuPont[™], Circleville, OH, USA) of 12 μm thickness was used as positron source sandwiched between two identical tested samples.

The raw PAL spectra were processed with LT 9.0 program.²³ Under unchanged contribution from a source (with 372 ps and ~2 ns inputs), these spectra were decomposed into two normalized components with $\tau_{1,2}$ lifetimes and $I_{1,2}$ intensities ($I_1+I_2=1$). Under above spectrometer resolution, this allows an error-bar for such arranged measuring protocol not worse than ± 0.005 ns in lifetimes and ± 0.01 in intensities. Introducing third component in the envelope of fitting curves did not improve goodness of fitting significantly (the bound positron-electron states were not proper for studied ChG in full agreement with previous results.²⁴⁻²⁶

(4) Positron trapping parameterization under two-state single-defect model

Assuming that x2-term reconstructed PAL spectrum represents positron trapping in one kind of defects (i.e. the positrons of $n_b(t)$ concentration annihilating from defect-free bulk state with λ_b rate, and the positrons of $n_d(t)$ concentration annihilating from defect-related state with λ_d rate being previously trapped by these defects with κ_d rate), and neglecting

competitive detrapping escape of positrons from defect state, the simplest set of kinetics equations can be written as (Fig. 1):¹³⁻¹⁸

$$\frac{dn_b(t)}{dt} = -(\lambda_b + \kappa_d)n_b(t), \quad (1)$$

$$\frac{dn_d(t)}{dt} = -\lambda_d n_d(t) + \kappa_d n_b(t), \quad (2)$$

where $n_b(t)$ and $n_d(t)$ are positron concentrations in bulk defect-free and defect states, respectively.

The full solution of the above set of eqs. under initial conditions $n_b(0)=1$ and $n_d(0)=0$ gives a normalized sum of negative exponentials with $\tau_{1,2}$ lifetimes and $I_{1,2}$ intensities (which are, in fact, the fitting parameters for experimentally measured raw PAL spectrum), where the longer lifetime τ_2 is the lifetime specific to the vacancy-type defect τ_d ($\tau_2=\tau_d$), while the shorter lifetime τ_1 is the “reduced bulk lifetime” (shorter in comparison with bulk non-trapped positron lifetime τ_b). The center of mass of the PAL spectrum coincides with average positron lifetime τ_{av} defined through normalized fractions of positron annihilations at defect-free bulk $\eta_b=\lambda_b \cdot (\lambda_b + \kappa_d)^{-1}$ and defect-specific $\eta_d=\kappa_d \cdot (\lambda_b + \kappa_d)^{-1}=\tau_1 \cdot \kappa_d$ states ($I_1+I_2=\eta_b+\eta_d=1$):

$$\tau_{av} = I_1\tau_1 + I_2\tau_2 = \eta_b\tau_b + \eta_d\tau_d. \quad (3)$$

Other physical quantities (the positron trapping modes), in part, the defect-free bulk positron lifetime τ_b and trapping rate in defects κ_d can be calculated from x2-term parameterized PAL spectra:

$$\tau_b = \tau_B = \frac{1}{\lambda_b} = \frac{\tau_1\tau_2}{I_1\tau_2 + I_2\tau_1}, \quad (4)$$

$$\kappa_d = I_2\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_d}\right). \quad (5)$$

In addition, the $(\tau_2-\tau_b)$ difference can be accepted as a size measure for extended free-volume defects where positrons are trapped, as well as the τ_2/τ_b ratio can be taken as direct

signature of nature of these trapping defects in terms of equivalent number of monovacancies.¹³

III. Results and discussion

(1) Input and optical examination of RE-doping in As-Sb selenide ChG

Input characteristics of the prepared ChG are gathered in Table 1.

It is known that partial As-by-Sb replacement within $\text{Ga}_y(\text{As}_{0.40-x}\text{Sb}_x\text{Se}_{0.60})_{100-y}$ cut-section reveals a stabilizing effect on ChG network suppressing parasitic crystallization processes caused by Ga addition.^{27,28} That is why the Sb-modified As_2Se_3 -based ChG will be examined, i.e. Ga-codoped arsenic selenide $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ and $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} .

As expected, the Sb addition causes increase in the ChG density ρ due to heavier atomic mass of Sb in comparison with As. The same tendency is observed for molar volume V_m showing lower atomic packing in Sb-contained ChG. No essential difference in both parameters is detected for RE-doped $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$. All samples under research remain in vitreous state, as it follows from character amorphous halos observed on XRD patterns centered near $2\theta = 16^\circ$, 30° and 55° . The glass stability factor $\Delta T=(T_x-T_g)$ defined from DSC measurements is reliably higher than 100°C for $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} , which serves as an indication that this glass is suitable for technological routes exploring re-heating procedures (like glass molding or fiber drawing).

Optical transmission and absorption cross-section spectra in Vis-NIR 800-2500 nm range for $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ and $\text{g-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} are shown in Fig. 2. In comparison to pure $\text{g-As}_2\text{Se}_3$ or $\text{g-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$,²¹ the Sb addition demonstrates a tendency to lower saturation level of optical transmittance due to increase in the refractive indices, since the electronic cloud of Sb is larger than that of As.²⁹ In addition,

the long-wave shift of optical absorption edge is observed with Sb adding, owing to its higher metallic behavior in respect to As, which decreases the optical band gap of ChG. No considerable changes are observed in optical transmission spectroscopy of un-doped and RE-doped $g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$, apart from appearance of Pr^{3+} -related absorption bands in the latter. Four absorption bands of Pr^{3+} are observed in the near-IR transmission region of doped ChG (see Fig. 2), these corresponding to inner-shell electron transitions of Pr^{3+} ions from the $^3\text{H}_4$ ground energy level to higher ones, in part $^3\text{F}_4$ (~1500 nm), $^3\text{F}_3$ (~1600 nm), $^3\text{F}_2$ (~2050 nm) and $^3\text{H}_6$ (~2300 nm).^{9,21}

The IR transmission and absorption cross-section spectra of un-doped and Pr-doped $g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ are presented on Fig. 3. These ChG are seen to possess excellent transparency up to 18 μm . Owing to higher atomic mass of Sb in comparison to As, the multiphonon cut-off in $g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ is shifted to lower energies in comparison with $g\text{-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$.²¹ Similarly to optical transmission in Vis-NIR spectral domain (Fig. 2), RE-doped and undoped ChG show no significant changes in their optical properties. One absorption band of Pr^{3+} ion is observed in mid-IR region near 4.5 μm , which can be ascribed to inner-shell electron transitions within Pr^{3+} ions from ground $^3\text{H}_4$ to higher $^3\text{H}_5$ energy level.

The low-temperature (liquid nitrogen $T=77\text{K}$) fluorescence spectra of $g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} is shown in Fig. 4. The observed broad-band fluorescence emission can be attributed to light absorption in the Urbach edge of *host* glassy matrix followed by non-radiative energy transfer to RE emitters, as it can be reasonably accepted for these ChG from previous research.^{30,31,32} The *host glass* luminescence due to deep states is eventually superimposed with emission originated from radiative transitions between electronic levels of Pr^{3+} ions. The strongest fluorescence

emission lines around 1000 nm on Fig. 4 correspond probably to $^3P_0-^1G_4$ and $^1G_4-^3H_4$ transitions, which are most noticeable for these RE ions excited at low temperature.³⁰

Thus, in full harmony with above characterization, we nominate the g-Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ as quite promising low-phonon energy *host* capable to successful fiber-optics applications.

(2) PAL response in RE-doping

Let's trace evolution of atomic-deficient free-volume structure of these ChG responsible for their functionality due to successful RE-doping, exploring the method of annihilating positrons.

The measured PAL spectra of the studied ChG were reconstructed from x2-term fitting route, these spectra for Ga-codoped g-Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ and this ChG doped with 500 wppm of Pr³⁺ being viewed on Fig. 5. The limited values of statistical scatter of variance tightly grouped along 0-axis testify that PAL measurements were adequately described within this fitting procedure. So decaying behavior of PAL spectra on Fig. 5 can be reflected by sum of two negative exponentials with different time constants inversed to positron lifetimes. The best-fit positron trapping modes for these ChG calculated within two-state trapping model¹³⁻¹⁸ are gathered in Table 2.

The x2-term decomposed PAL spectrum of parent stoichiometric g-As₂Se₃ demonstrates defect-related lifetime $\tau_2=0.360$ ns (Table 2), which is proper to this ChG studied previously.³³⁻³⁶ In general, the positron trapping in this ChG is defined by trapping rate $\kappa_t=0.92$ ns⁻¹ occurring under fraction of trapped positrons $\eta_d=0.19$. In respect to Jensen's et al. DFT-calculations reliably approbated for orthorhombic As₂Se₃ structure,³⁵ this $\tau_2=0.360$ ns lifetime gives an estimate for related volume of positron-trapping sites near 92 \AA^3 . This open volume corresponds to 0.10 ns in $(\tau_2-\tau_b)$ difference and 1.39 in τ_2/τ_b ratio, which can be

Accepted Article

accepted as a signature of rather extended triple-quadruple vacancies. Nevertheless, it is difficult to define which part of this overall free volume is really atomic-accessible in glassy network in view of complicated inner structural configuration composed of atom-shared trigonal $\text{AsSe}_{3/2}$ pyramids interlinked by $=\text{As-Se-As}=\text{}$ bridges without essential content of homonuclear As-As and Se-Se bonds (the sketch of typical structural network of $\text{g-As}_2\text{Se}_3$ is given in Fig. 6a).⁵ Preferential process of positron trapping in such glassy matrix is defined by extended free-volume spaces near Se atoms neighboring with $\text{AsSe}_{3/2}$ polyhedrons.^{34,35} Because of directionality of covalent bonding in ChG, the Se atoms form lower-electron density spaces also known as *bond free solid angles* (BFSA) in terms of Kastner.³⁷ These *atomic-inaccessible BFSA* contribute to neighboring geometrical free volumes, ensuring an effective negative electrical charge due to proximity with electronegative Se atoms linked with more electropositive As or Sb atoms. So, the BFSA around Se atoms form an outer wall for innermost free-volume geometrical voids, which can be identified in view of their preferential electric state as counterparts of cation-type vacancies in crystals.¹³ Therefore, the most efficient positron traps in $\text{g-As}_2\text{Se}_3$ can be imaged as free-volume voids formed within *cycle-type arrangement* of corner-sharing $\text{AsSe}_{3/2}$ pyramids, composed of atomic-accessible geometrical holes arrested by surrounding atomic-inaccessible Se-based BFSA. The plane projection of such atomic-deficient structure character for $\text{g-As}_2\text{Se}_3$, where A-marked free-volume voids are supposed among others (B- and C-marked) as governing sites for positron trapping is depicted on Fig. 6a.

However, this glassy network with highly saturated covalent bonding does not satisfy condition of electrical charge compensation for RE ions to be embedded in electrically active RE^{3+} state. This can be achieved for Ga-codoped ChG, i.e. glasses modified by Ga (alternatively In) additions.⁶⁻¹⁰

Effect of Ga-codoping in g-As₂Se₃, i.e. transition from g-As₂Se₃ to g-Ga₂(As_{0.40}Se_{0.60})₉₈, is revealed through gradual dropping in the I_2 intensity accompanied by lifting in defect-specific lifetime τ_2 to 0.382 ns (see Table 2). At the basis of Jensen's et al.³⁵ formalism, the latter can be ascribed to inner free volumes reaching as high as $\sim 110 \text{ \AA}^3$. This result is in obvious contrast to Ga-modified g-Te₂₀As₃₀Se₅₀ ChG (known as TAS-235 glass),^{24,25} where defect-specific positron lifetime τ_2 was rather unchanged under Ga-codoping. Such specifics can be reasonably explained by structural changes in a glassy network due to rearrangement in local chemical bonding introduced by incorporated Ga codopants. With Ga codoping in TAS-235 glass, when Ga atoms replace As ones within Te₂₀(As/Ga)₃₀Se₅₀ cut-section, the glassy network generally maintains the native average atomic coordination $Z=2.30$, thus ensuring unchanged values of τ_2 lifetime regardless Ga content. In the current case of g-Ga₂(As_{0.40}Se_{0.60})₉₈, the glassy network enlarges its average atomic coordination from $Z=2.40$ (for g-As₄₀Se₆₀) to $Z=2.412$. Distinct jump in defect-specific τ_2 lifetime is known to occur under such compositional variation in g-As-Se system,^{16,33,34} caused by increased number of overlapped free-volume voids (i.e. BFSA) compactly grouped around end-terminated Se atoms within bridging Se_{2/2}-As-As-Se_{2/2} structural units.³⁶

Thus, the Ga-codoping in g-As₂Se₃ results in *agglomeration* of existing free-volume voids (increase in their volume, but decrease in their content), thus leading to gradual decrease in the positron trapping rate in defects κ_d and, correspondingly, the fraction of trapped positrons η_d (Table 2).

In general, such compositional modification when only atomic-deficient structure is changed, is meaningless to accommodate RE ions obeying electrically-active RE³⁺ state, so avoiding non-radiative decay due to ion-ion interaction, RE-ion clustering and/or glass devitrification.^{3,8,25,26} The nearest atomic environment of free-volume voids accommodated RE dopants have to adopt a local excess of positive electrical charge to ensure compensation

throughout a glassy matrix. Successful resolution of this problem is just based on the possibility of Ga-codopants to reveal their metallic behavior being inserted in a covalent-bonded ChG network. In interaction with chalcogens, the Ga atoms create some polyhedrons, which are, from one side, topologically consistent with principal network-forming polyhedrons to attain unique cycle-type arrangement having a large number of character voids, but, from other side, these codopants are able to stabilize some electrical charge imbalance owing to local chalcogen (Se) over-coordination around Ga atoms.^{8,10,38}. Therefore, under transition to $g\text{-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$, the $\text{GaSe}_{4/2}$ tetrahedrons with energetically favorable Ga-Se bonds appear in a network of corner-shared trigonal $\text{AsSe}_{3/2}$ pyramids forming characteristic cycle-atomic arrangement of $g\text{-As}_2\text{Se}_3$ (see Fig. 6b). This structure is not disturbed essentially under condition of small amount of Ga codopant added, apart from some homonuclear As-As bonds (red-distinguished on Fig. 6b), which appear to compensate lack of Se atoms in $=\text{As-Se-As}=\text{ bridges}$. However, excess of these anion-type atoms occupying Se^{2-} states in cation-centered $\text{GaSe}_{4/2}$ tetrahedrons (shown by blue-covered circles on Fig. 6b) causes the cloud of preferentially negative electrical charge for whole neighboring void. In such a way, the negatively-charged void entities of slightly increased volume in Ga-modified ChG serve as precursors for *charge-compensating incorporation* of electrically active RE^{3+} ions.

One of expected parasitic drawbacks of Ga-codoping is related to potentially enhanced crystallization ability in Ga-contained ChG under RE doping, since both Ga and RE chalcogenides possess isostructural crystalline polymorphs.^{3,21} In case of As-based ChG prepared by conventional melt-quenching route, this obstacle can be suppressed under partial As-to-Sb replacement. This was a reason to decline our attention from $g\text{-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$ to more vitreous $g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$. In respect to atomic-deficient structure evidenced from PAL spectroscopy, this Sb-substituted ChG demonstrates partial recovery to pure g -

As₄₀Se₆₀. Indeed, in this g-Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈, the defect-specific lifetime τ_2 is depressed to 0.363 ns and second component intensity I_2 is elevated to 0.422, thus resulting in steadily increasing positron trapping rate in defects with $\kappa_d=0.85$ ns⁻¹ (see Table 2). This Sb-modification effect is not accompanied by change in the defect type, since neither ($\tau_2-\tau_b$) difference, nor τ_2/τ_b ratio remain constant within measuring error-bar. Such changes are supposed to be defined by increase in the atomic packing of glass-forming network due to heavier Sb atoms appeared in cation sub-system instead of As atoms, which also cause increase in the atomic density ρ from 4.64 to 4.90 g/cm³ for g-Ga₂(As_{0.40}Se_{0.60})₉₈ and g-Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈, respectively.

Thus, effect of RE-doping on PAL modes can be simply explained in terms of *competitive contribution of changed occupancy sites* available for RE ions and trapped positrons in the modified structure of Ga-codoped ChG. Indeed, from the point of affinity to negative electrical charge attached to neighboring free-volume space, the same type of voids, which can accommodate RE³⁺ ions as shown in Fig. 6b, can be also attractive sites for annihilating positrons.¹³⁻¹⁸ Under RE doping, the positively-charged Pr³⁺ ions are stabilized in a glassy network due to strong Pr³⁺-Se-Ga covalent bridges,^{8,39,40} thus eliminating corresponding negatively-charged voids (A-marked on Fig. 6) as potential positron traps as it is shown in Fig. 6c. This process results in reduced positron trapping rate in defects κ_d originated from essential decrease in second component intensity I_2 (and content of these defects, as it can be expected for such measuring conditions) and rather slight increase in defect-specific lifetime τ_2 (Table 2), meaning that void volume is not essentially altered under RE doping.

Concentration of these free-volume defects responsible for positron trapping in RE-doped ChG can be estimated accepting their analogy with negative cation-type vacancies in semiconductors giving trapping coefficients of approximately 10^{15} atom·s⁻¹.¹³ With atomic

Accepted Article

densities (gathered in Table 1) and experimental positron trapping rates for different ChG (Table 2), this estimation gives defect concentration close to $\sim 5 \cdot 10^{16} \text{ cm}^{-3}$. It means that under a condition of full identity to void occupation for both annihilating positrons and RE-ions, the effect of RE doping can be detected at very low concentration level (reaching only tens of wppm). That is why the PAL spectroscopy can be successfully applied to study RE doping in glassy substances, where conventional atomic-sensitive probes such as X-ray, electron or neutron diffraction are ineffective because of under-margin content of embedded ions, which is typically beyond reliably detectable limits of these methods.

IV. Conclusions

Free-volume structure of arsenic selenide As_2Se_3 glass modified with Sb (substituting As) and codoped with Ga to $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ composition is traced by annihilating positrons in lifetime measuring mode treated in terms of two-state trapping model. The most efficient positron traps in parent As_2Se_3 glass are shown can be imaged as free-volume voids formed within cycle-type arrangement of directly corner-sharing trigonal $\text{AsSe}_{3/2}$ pyramids, composed of atomic-accessible geometrical holes arrested by surrounding atomic-inaccessible Se-based bond-free solid angles. Positron trapping is mostly depressed in Ga-codoped $\text{Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$ glass due to agglomeration of free-volume voids, thus leading to gradual decrease in trapping rate and fraction of trapped positrons. Partial As replacement by heavier Sb atoms to form $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ glass occurs stabilizing effect on rare-earth doping, partially recovering void structure of parent glass with increased trapping in defects. Effect of 500 wppm of Pr^{3+} incorporated in $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ glass is explained in terms of competitive contribution of changed occupancy sites available for rare-earth ions and annihilating positrons being trapped in Ga-modified glassy network. Under doping, the Pr^{3+} ions are stabilized due to Pr^{3+} -Se-Ga linkages, thus eliminating neighboring void as

potential positron trapping sites. Effect of rare-earth doping in the studied glass results in notably reduced positron trapping rate in free-volume voids, originated from their decreased content and rather slightly altered volume.

Acknowledgements

With a great pleasure I thank to Roman Golovchak (Austin Peay University, TN, USA) for his helpful assistance with fluorescence measurements. The valuable consulting on PALS experiments provided by Dr. Adam Ingram (Opole University of Technology) is also highly acknowledged. B. Bureau, C. Boussard-Pledel and V. Nazabal (Glass and Ceramics laboratory of University of Rennes 1) are acknowledged for their valuable discussion regarding presented results.

References

- ¹J.-L. Adam, X. Zhang (Eds.), *Chalcogenide Glasses: Preparation, Properties and Applications*, Woodhead Publishing, Oxford, Cambridge, New Dehli, 2014.
- ²S. Cui, R. Chahal, Ya. Shpotyuk, C. Boussard, J. Lucas, F. Charpentier, H. Tariel, O. Loreal, V. Nazabal, O. Sire, V. Monbet, Z. Yang, P. Lucas, B. Bureau, “Selenide and telluride glasses for mid-infrared bio-sensing,” *Proc. SPIE*, **8938** 893805-1-9 (2014).
- ³A.B. Seddon, Z. Tang, D. Furniss, S. Sujecki and T.M. Benson, “Progress in rare-earth-doped mid-infrared fiber lasers,” *Opt. Express*, **18** 26704-26719 (2010).
- ⁴N.F. Mott, E.A. Davis, *Electron Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979.
- ⁵A. Feltz, *Amorphous and vitreous inorganic solids*, Mir, Moscow, 1986.
- ⁶B. Cole, L.B. Shaw, P.C. Pureza, R. Mossadegh, J.S. Sanghera and I.D. Aggarwal, “Rare-earth doped selenide glasses and fibers for active applications in the near and mid-IR,” *J.*

Non-Cryst. Solids, **256-257** 253-259 (1999).

⁷J. Hu, C.R. Menyuk, C. Wei, B. Shaw, J.S. Sanghera and I.D. Aggarwal, "Highly efficient cascaded amplification using Pr³⁺-doped mid-infrared chalcogenide fiber amplifiers," *Opt. Lett.*, **40** 3687-3690 (2015).

⁸B.G. Aitken, C.W. Ponader and R.S. Quimby, "Clustering of rare earths in GeAs sulfide glass," *C.R. Chimie*, **5** 865-872 (2002).

⁹M.F. Churbanov, I.V. Scribachev, V.S. Shiryaev, V.G. Plotnichenko, S.V. Smetanin, E.B. Kryukova, Yu.N. Pyrkov and B.I. Galagan, "Chalcogenide glasses doped with Tb, Dy and Pr ions," *J. Non-Cryst. Solids*, **326-327** 301-305 (2013).

¹⁰R. Golovchak, Ya. Shpotyuk, V. Nazabal, C. Boussard-Pledel, B. Bureau, J. Cebulski, H. Jain, "Study of Ga incorporation in glassy arsenic selenides by high-resolution XPS and EXAFS," *J. Chem. Phys.*, **142** 184501-1-10 (2015).

¹¹J. Kullmann, D. Enke, S. Thraenert, R. Krause-Rehberg, M. Beiner, "Characterization of pore filling of mesoporous host systems by means of positronium annihilation lifetime spectroscopy (PALS)," *Opt. Appl.*, **42** 281-286. (2012).

¹²A.J. Hill, B.D. Freeman, M. Jaffe, T.C. Merkel and I. Pinnau, "Tailoring nanospace," *J. Mol. Struct.*, **739** 173-178 (2005).

¹³R. Krause-Rehberg and H. Leipner, *Positron annihilation in semiconductors: defect studies*, Springer, Heidelberg, 1999.

¹⁴Y.C. Jean, P.E. Mallon, D.M. Schrader, *Principles and Application of Positron and Positronium Chemistry*, World Sci. Publ. Co. Pte. Ltd., New Jersey-London-Singapore-Hong Kong, 2003.

¹⁵F. Tuomisto and I. Makkonen, "Defect identification in semiconductors with positron annihilation: Experiment and theory," *Rev. Mod. Phys.*, **85** 1583-1631 (2013).

- ¹⁶O. Shpotyuk and J. Filipecki, *Free volume in vitreous chalcogenide semiconductors: possibilities of positron annihilation lifetime study*, WSP, Czestochowa, 2003.
- ¹⁷A. Seeger, "The study of defects in crystals by positron annihilation," *Appl. Phys.*, **4** 183-199 (1974).
- ¹⁸D.J. Keeble, U. Brossmann, W. Puff, and R. Würschum, in *Characterization of materials*, E.N. Kaufmann (Ed.), John Wiley & Sons, Inc.; New York, 2012, p. 1899-1925.
- ¹⁹Ya. Shpotyuk, B. Bureau, C. Boussard-Pledel, V. Nazabal, R. Golovchak, P. Demchenko, I. Polovynko, "Effect of Ga incorporation in the $As_{30}Se_{50}Te_{20}$ glass," *J. Non-Cryst. Solids*, **398-399** 19-25 (2014).
- ²⁰O. Shpotyuk, A. Ingram, B. Bureau, Ya. Shpotyuk, C. Boussard-Pledel, V. Nazabal, R. Szatanik, "Positron annihilation probing of crystallization effects in TAS-235 glass affected by Ga additions," *J. Phys. Chem. Solids*, **75** 1049-1053 (2014).
- ²¹Ya. Shpotyuk, C. Boussard-Pledel, V. Nazabal, R. Chahal, J. Ari, B. Pavlyk, J. Cebulski, J.L. Doualan, B. Bureau, "Ga-modified As_2Se_3 -Te glasses for active applications in IR photonics," *Opt. Mater.*, **46** 228-232 (2015).
- ²²A. Hrubý, "Evaluation of glass-forming tendency by means of DTA," *Czech. J. Phys. B*, **22** 1187-1193 (1972).
- ²³J. Kansy, "Microcomputer program for analysis of positron annihilation lifetime spectra," *Nucl. Instrum. Methods Phys. Res., Sect. A*, **374** 235-244 (1996).
- ²⁴Ya. Shpotyuk, A. Ingram, O. Shpotyuk, A. Dziedzic, C. Boussard-Pledel, B. Bureau, "Free-volume nanostructurization in Ga-modified As_2Se_3 glass," *Nanoscale Res. Lett.*, **11** 20-1-7 (2016).
- ²⁵Ya. Shpotyuk, A. Ingram, O. Shpotyuk, C. Boussard-Pledel, V. Nazabal, B. Bureau, "Effect of rare-earth doping on the free-volume structure of Ga-modified $Te_{20}As_{30}Se_{50}$ glass," *RSC Adv.*, **6** 22797-22802 (2016).

²⁶Ya. Shpotyuk, A. Ingram and O. Shpotyuk, "PAL spectroscopy of rare-earth doped Ga-Ge-Te/Se glasses. Journal of Physics and Chemistry of Solids," *J. Phys. Chem. Solids*, **91** 76-79 (2016).

²⁷Ya. Shpotyuk, C. Boussard-Pledel, V. Nazabal, B. Bureau, "The influence of Sb on glass forming ability of Ga-containing As₂Se₃ glasses," *J. Am. Ceram. Soc.*, DOI: 10.1111/jace.14662.

²⁸E. Cernoskova, J. Holubova, B. Bureau, C. Roiland, V. Nazabal, R. Todorov, Z. Cernosek, "Thermoanalytical properties and structure of (As₂Se₃)_{100-x}(Sb₂Se₃)_x glasses by Raman and ⁷⁷Se MAS NMR using a multivariate curve resolution approach," *J. Non-Cryst. Solids*, **432** 426-431 (2016).

²⁹J. Musgraves, N. Carlie, L. Petit, K. Richardson, G. Boudebs, J. Choi, M. Richardson, "Effect of replacement of As by Ge and Sb on the photo-response under near infrared femtosecond laser irradiation in As-based sulfide glasses," *Intern. J. Appl. Glass Sci.*, **2** 308-320 (2011).

³⁰J. Zavadil, P. Kostka, J. Pedlikova, Z.G. Ivanova, K. Zdansky, "Investigation of Ge based chalcogenide glasses doped with Er, Pr and Ho," *J. Non-Cryst. Solids*, **356** 2355-2359 (2010).

³¹S.Q. Gu, S. Ramachandran, E.E. Reuter, D.A. Turnbull, J.T. Verdeyen, S.G. Bishop, "Photoluminescence and excitation spectroscopy of Er-doped As₂S₃ glass: Novel broad band excitation mechanism," *J. Appl. Phys.*, **77** 3365-3371 (1995).

³²S.G. Bishop, D.A. Turnbull, B.G. Aitken, "Excitation of rare earth emission in chalcogenide glasses by broadband Urbach edge absorption," *J. Non-Cryst. Solids*, **266-269** 876-883 (2000).

³³O.K. Alekseeva, V.I. Mihailov, A.P. Chernov, V.P. Shantarovich, "Point structural defects studied in chalcogenide semiconductors by positron annihilation," *Sov. Fiz. Tverd. Tela*, **19** 3452-3454 (1977).

³⁴O.K. Alekseeva, V.I. Mihajlov, V.P. Shantarovich, “Positron annihilation in point defects of the glassy As-Se system,” *Phys. Stat. Solidi A*, **48** K169-K173 (1978).

³⁵K.O. Jensen, P.S. Salmon, I.T. Penfold, P.G. Coleman, “Microvoids in chalcogenide glasses studied by positron annihilation,” *J. Non-Cryst. Solids*, **170** 57-64 (1994).

³⁶A. Ingram, R. Golovchak, M. Kostrzewa, S. Wacke, M. Shpotyuk, O. Shpotyuk, “Compositional dependences of average positron lifetime in binary As-S/Se glasses,” *Phys. B*, **407** 652-655 (2012).

³⁷M. Kastner, “Compositional trends in the optical properties of amorphous lone-pair semiconductors,” *Phys. Rev. B*, **7** 5237-5252 (1973).

³⁸R. Golovchak, Ya. Shpotyuk, C.M. Thomas, V. Nazabal, C. Boussard-Pledel, B. Bureau, H. Jain. “Peculiarities of Ga and Te incorporation in glassy arsenic selenides,” *J. Non-Cryst. Solids*, **429** 104-111 (2015).

³⁹T.H. Lee, S.I. Simdyankin, L. Su and S.R. Elliott, “Evidence of formation of tightly bound rare-earth clusters in chalcogenide glasses and their evolution with glass composition,” *Phys. Rev. B*, **79** 180202-1-4 (2009).

⁴⁰T.H. Lee, S.I. Simdyankin, J. Hegedus, J. Heo, S.R. Elliott, “Spatial distribution of rare-earth ions and GaS₄ tetrahedra in chalcogenide glasses studied via laser spectroscopy and ab initio molecular dynamics simulation,” *Phys. Rev. B*, **81** 104204-1-6 (2010).

Figures caption list:

Fig. 1. Two-state positron trapping model with a single free-volume vacancy.

Fig. 2. Vis-NIR transmission and absorption cross section spectra of Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ and Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ + 500 wppm of Pr samples.

Fig. 3. IR transmission and absorption cross section spectra of Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ and Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ + 500 wppm of Pr samples.

Fig. 4. Low-temperature fluorescence spectra of Ga₂(As_{0.28}Sb_{0.12}Se_{0.60})₉₈ doped with 500 wppm of Pr³⁺. Intensity of fluorescence (a.u.) is given by color map at the right. Straight

(grey) lines are caused by Rayleigh scattering of the excitation light (ignored during analysis).

Fig. 5. Raw PAL spectra of Ga-codoped $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ (a) and $\text{Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ doped with 500 wppm of Pr^{3+} (b). The bottom insets show statistical scatter of variance.

Fig. 6. Sketch of plane projection of atomic-deficient void structure of $g\text{-(As/Sb)}_2\text{Se}_3$ built of corner-sharing $(\text{As/Sb})\text{Se}_{3/2}$ pyramids showing character cycle-type arrangement with free-volume voids in Ga-free (a), Ga-codoped (b) and RE-modified Ga-codoped (c) glass-forming network (see text for more details).

Table 1. Input characterization of $g\text{-Ga}_x[(\text{As/Sb})_{0.40}\text{Se}_{0.60}]_{100-x}$

ChG composition	Z	ρ	V_m	T_g	T_x	ΔT
		g/cm^3	cm^3/mol	$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$
$g\text{-As}_{40}\text{Se}_{60}$	2.400	4.619	16.74	184	---	---
$g\text{-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$	2.412	4.635	16.66	182	307	125
$g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$	2.412	4.900	16.88	191	---	---
$g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ with 500 wppm Pr^{3+}	2.412	4.890	16.95	195	307	112

Table 2. Fitting parameters and positron trapping modes describing two-component reconstructed PAL spectra in $g\text{-Ga}_x[(\text{As/Sb})_{0.40}\text{Se}_{0.60}]_{100-x}$

ChG sample	Fitting parameters			Positron trapping modes					
	τ_1	τ_2	I_2	$\tau_{av.}$	τ_b	κ_d	$\tau_2 - \tau_b$	τ_2/τ_b	η_d
	ns	ns	a.u.	ns	ns	ns^{-1}	ns	-	-
$g\text{-As}_{40}\text{Se}_{60}$	0.210	0.360	0.462	0.279	0.260	0.92	0.10	1.39	0.19
$g\text{-Ga}_2(\text{As}_{0.40}\text{Se}_{0.60})_{98}$	0.223	0.382	0.401	0.287	0.267	0.75	0.11	1.43	0.17
$g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$	0.210	0.363	0.422	0.274	0.255	0.85	0.11	1.42	0.18
$g\text{-Ga}_2(\text{As}_{0.28}\text{Sb}_{0.12}\text{Se}_{0.60})_{98}$ with 500 wppm of Pr^{3+}	0.218	0.374	0.376	0.276	0.258	0.72	0.12	1.45	0.16







