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Oleh Shpotyuk[a,b], Adam Ingram[c], Zdenka Bujňáková[d], Peter Baláž[d], Yaroslav Shpotyuk[e,f], Catherine Boussard-Pledel[g], and Bruno Bureau[g]

[a]*Jan Dlugosz University in Czestochowa, 13/15, al. Armii Krajowej, Czestochowa, 42200, Poland*
[b]*Vlokh Institute of Physical Optics, 23, Dragomanov str., Lviv, 79005, Ukraine*
[c]*Opole University of Technology, 75, Ozimska str., Opole, 45370, Poland*
[d]*Institute of Geotechnics of Slovak Academy of Sciences, 45, Watsonova str., Košice, 04001, Slovakia*
[e]*University of Rzeszow, 1, Pigonia str., 35-310 Rzeszow, Poland*
[f]*Ivan Franko National University of Lviv, 1, Universytetska str., 79000, Lviv, Ukraine*
[g]*Laboratoire Verres et Céramiques UMR-CNRS 6226, University of Rennes 1, Rennes Cedex, 35042, France*

Abstract. Atomic-deficient void structure is studied in nanocomposites prepared by mechanochemical milling of glassy g-As$_2$Se$_3$ in a water solution of polyvinylpyrrolidone (PVP) employing positron annihilation lifetime spectroscopy. Formalism of Ps-to-positron trapping conversion known as x3-x2-CDA (coupling decomposition algorithm) is applied to identify free-volume defects in the pelletized g-As$_2$Se$_3$/PVP nanocomposite in respect to dry-milled g-As$_2$Se$_3$ one. Under wet-milling, the inter-nanoparticle Ps-decaying sites in preferential PVP environment replace free-volume positron traps (in dry-milled g-As$_2$Se$_3$) with defect-specific lifetime of 0.352 ns, corresponding to di-/tri-atomic vacancies in g-As-Se.

Keywords:, arsenic selenide, free-volume defect, nanoparticle, nanocomposite, positron annihilation, mechanical milling.
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INTRODUCTION

The chalcogenide compounds represented by As$_2$S$_3$, different As$_4$S$_4$ polymorphs, and As$_2$O$_3$, the overall known as arsenicals [1], have attracted a tight attention in scientific community because of their potential application as promising anti-cancer drugs in treatment of hematological malignant diseases [2]. Their medicinal activity can be tuned by *nanostructurization* stretching over atomic and sub-atomic length-scales [3-6] due to mechanochemistry, an advanced instrumentation tool ensuring arsenicals with unprecedented biocompatibility via enhanced ratio of surface-to-bulk states [7]. In medicinal implementations, the mechanically milled (MM) arsenicals are combined with organic stabilizers such as polyvinylpyrrolidone (PVP), to keep individuality of created nanoparticles (NPs), thereby producing *PVP-capped arsenical nanocomposites* [5,6,8-10]. Nowadays, there are no comparative information concerning similar functionalization in other types of arsenicals, such as arsenic selenides As-Se, forming a large group of glassy-like media possessing widespread application in IR photonics [11].

In this work, the free-volume structural arrangement in the PVP-encapsulated glassy g-As$_2$Se$_3$ nanocomposites prepared by high-energy wet attrition ball milling is studied employing positron annihilation lifetime (PAL) spectroscopy, the non-destructive experimental probe for nanostructurization in composite materials [10,12,13].

EXPERIMENTAL

Nanocomposite preparation and characterization

The studied nanocomposites were prepared using coarse-grained pieces of bulk g-As$_2$Se$_3$ synthesized from high-purity commercial elemental precursors (As and Se of 5N purity). The plane-parallel plates (1.0-1.5 mm in a

thickness) cut from thermally-annealed glassy ingots and polished to a high optical quality were used as reference samples for PAL spectroscopy measurement. The synthesized g-As$_2$Se$_3$ has 4.590 g·cm^{-3} density determined at room temperature by the Archimedes displacement technique in ethanol, and mid-onset glass-transition temperature T$_g$=185°C determined from DSC scans, as typical values proper to g-As$_2$Se$_3$ [11].

The high-energy milling was performed in both dry and wet modes. The dry-mode milling was performed in Pulverissete 6 mill (operated at 500 rpm rotational speed and protective argon atmosphere) for 20 min in 250 mL tungsten carbide chamber (loaded with 50 tungsten carbide balls each having 10 mm in diameter), using 3 g of coarse-grained g-As$_2$Se$_3$ preliminary sieved under 200 μm. After milling, the powder was compressed by compacting inside a stainless steel die under a pressure of ~0.7 GPa to produce the dry-MM g-As$_2$Se$_3$ pellets having near 6 mm in a diameter and 1 mm in a thickness. The part of dry-milled powder was treated in a wet-milling mode. This 90-min attrition ball milling route performed in a presence of 300 mL of 0.5% PVP solution in laboratory MiniCer mill (Netzsch, Germany), operated under protective argon atmosphere at 3500 rpm speed (85% loading of milling shaft with yttrium-stabilized ZrO$_2$ balls, each having 0.6 mm in a diameter). For this purpose, we used the powdered PVP with an average molecular weight of 40 000 g·mol^{-1} purchased from Sigma-Aldrich Co. LLC (St. Louis, MO, USA). After filtration through sterile 0.22 μm filter, the separated solid phase was dried at 70°C and pelletized under the same pressure of ~0.7 GPa, thus producing the g-As$_2$Se$_3$/PVP- nanocomposite.

The NPs sizes in milled arsenicals detected by photon cross-correlation spectroscopy reveal typical single modal distribution with d$_{50}$=182 nm (i.e. 50% of NPs were smaller than 182 nm) and d$_{99}$=267 nm (i.e. 99% of NPs were smaller than 267 nm). As it follows from X-ray diffractometry, the high-energy attrition ball milling in the above conditions does not change amorphous state of the substance.

PAL spectra recording

The PAL spectra were recorded with fast-fast coincidence system (ORTEC) of 230 ps resolution stabilized at 22°C and relative humidity of 35%. To ensure precise lifetime measurement, each PAL spectrum was recorded in normal-measurement statistics (~10^6 coincidences), the channel width of 6.15 ps allowing 8000 channels in a total. The ^{22}Na isotope of ~50 kBq activity prepared from aqueous ^{22}NaCl solution (wrapped by Kapton$^®$ foil of 12 μm thickness and sealed) was used as positron source sandwiched between two identical samples. The source correction (12% component contribution with 0.372 ns lifetime installed due to calibration with Ni and Kapton$^®$ foil) was applied to compensate input originating from annihilation in the source itself and in the covering Kapton$^®$ foil. The best fitting of the PAL spectra was achieved with LT 9.0 program [20] under decomposition into three single exponentials), covering channels from positrons annihilating in (i) defect-free bulky states, (ii) trapped in extended free-volume defects (positron-trapping sites) and (iii) forming bound positron-electron Ps (positronium) state. The error-bar in positron lifetimes τ_i and intensities I_i were ±0.005 ns and 0.5%, respectively. The PAL data were treated using two-state simple trapping model (STM), assuming one kind of free-volume defects for positrons [12,15,16], disturbed by slight input from Ps-decaying. This approach allows determination of positron trapping modes (defect-specific τ_d and defect-free bulk τ_b lifetimes, trapping rate in defects κ_d,) under condition of slight input from Ps-decaying modes (i.e. radius of spherical holes R and fractional free volume f_v).

PAL spectra treatment with x3-x2-CDA

For inhomogeneous solids, where annihilation is expected through mixed positron-Ps channels so that only Ps-traps are transformed in positron-trapping centers (and vice versa), the formalism of Ps-to-positron trapping conversion [5,6,13] can be applied to identify free-volume defects. Within this approach referred to as x3-x2-CDA (coupling decomposition algorithm) [13], we deal with x3-term PAL spectrum transformed to generalized x2-term form for both reference and nanostructurized solids (caused, in part, by incorporation of *guest* NPs in *host* matrix), the second component involving all possible positron-trapping and Ps-decaying contributions. This approach allows resolving additional input with defect-specific τ_{int} lifetime and I_{int} intensity in the second component of reconstructed x2-term PAL spectrum, provided compensating (τ_n,I_n) input in the first component obeys complete equilibrium [13]. Parameterization of Ps-to-positron trapping conversion in the nanostructurized matrix is achieved accepting (τ_n,I_n) and (τ_{int},I_{int}) as first and second components of x2-term PAL spectrum employing two-state STM [12,15]. The trapping modes derived within this approach include defect-specific τ_{int} and defect-free bulk τ_b^{NP} lifetimes, trapping rate in defects κ_d^{NP}, signature of trap size in terms of equivalent number of vacancies defined by (τ_{int}-τ_b^{NP}) difference and nature of these traps defined by τ_{int}/τ_b^{NP} ratio [12].

RESULTS AND DISCUSSION

The PAL spectra of pelletized dry-MM and wet-MM g-As$_2$Se$_3$, and bulk g-As$_2$Se$_3$ are built of three single exponentials (Table 1), the corresponding PAL trapping parameters being gathered in Table 2.

TABLE 1. PAL spectra fitting of g-As$_2$Se$_3$-based arsenicals within free x2- and x3-term decomposition.

Arsenical sample (fitting procedure)	[FIT-1]	PAL spectra fitting parameters					$\tau_{av.}$
		τ_1	τ_2	τ_3	I_2	I_3	ns
		ns	ns	ns	a.u.	a.u.	
Bulk g-As$_2$Se$_3$ (x2-term)	0.07	0.209	0.363	-	0.627	-	0.305
Bulk g-As$_2$Se$_3$ (x3-term)	0.01	0.193	0.358	2.091	0.620	0.007	0.310
Dry-MM g-As$_2$Se$_3$ (x3-term)	0.05	0.202	0.371	2.087	0.540	0.015	0.322
Wet-MM g-As$_2$Se$_3$ (x3-term)	0.07	0.212	0.428	1.891	0.400	0.052	0.386

The PAL spectrum of reference bulky g-As$_2$Se$_3$ sample decomposed on three free exponentials reveals second component with τ_2 lifetime approaching ~0.36 ns, which is at a character level of triple- and quadruple-type vacancies in As-Se matrix [17-19]. The third component with relatively small fractional free volume f_v=0.15 and τ_3=2.091 ns can be ascribed to Ps-related holes having a radius of 0.296 nm. Despite small number of corresponding Ps-decaying sites, this component cannot be eliminated from the PAL spectrum without notable reduction in fitting goodness. Nevertheless, we also decomposed the measured PAL spectrum of bulky g-As$_2$Se$_3$ in evidently worse x2-term form (due to seven-times increased [FIT-1] value), to compare these results with known data for the same glass treated within two-state STM [12,15]. The good coincidence in defect-specific τ_d and defect-free bulk τ_b lifetimes, as well as trapping rate in defects κ_d speaks in a favor of tight proximity between these reference samples.

TABLE 2. PAL trapping modes of g-As$_2$Se$_3$-based arsenicals within free x2- and x3-term decomposition

Arsenical sample	Positron-trapping modes						Ps-decay modes	
	$\tau_{av.}^{tr}$	τ_b	κ_d	$\tau_2-\tau_b$	τ_2/τ_b	η	R_3	f_v^3
	ns	ns	ns^{-1}	ns	a.u.	a.u.	nm	%
Bulk g-As$_2$Se$_3$ (x2-term)	0.305	0.285	1.27	0.08	1.27	0.27	-	-
Bulk g-As$_2$Se$_3$ (x3-term)	0.297	0.272	1.51	0.09	1.32	0.29	0.296	0.15
Dry-MM g-As$_2$Se$_3$ (x3-term)	0.295	0.270	1.24	0.10	1.37	0.25	0.296	0.29
Wet-MM g-As$_2$Se$_3$ (x3-term)	0.304	0.270	1.01	0.16	1.58	0.21	0.277	0.83

In structurally inhomogeneous substances composed of agglomerated NPs having individual 100-300 nm grains (as it clearly illustrated by particle size distribution on Fig. 1), the large fraction of positrons thermalized inside these grains travelers towards grain boundaries (because of their diffusion length becomes comparable with NP size), where they annihilate after getting trapped into free-volume defects. This feature determines a more complicated PAL spectroscopy for both dry-MM and wet-MM g-As$_2$Se$_3$ (as compared with non-milled bulky samples) in addition to large amount of free-volume voids and unfilled cavities created due to powdering these arsenicals [20].

The x3-term decomposed PAL spectrum of the pelletized dry-MM g-As$_2$Se$_3$ demonstrates slightly increased defect-specific lifetime τ_2, but rather unchanged Ps-decaying lifetime τ_3, the average lifetime $\tau_{av.}$ as a mass center of all positron-annihilation events [12] being only slightly shifted from 0.310 ns to 0.322 ns. The third component intensity I_3 is over two-times increased as in bulky g-As$_2$Se$_3$, resulting in equivalent growth of fractional free volume f_v (Table 2). The relative stability of average lifetime $\tau_{av.}$ in this arsenical is evidently counter-balanced by abruptly decreased second component intensity I_2, the process favoring changes in the Ps-formation probability [21].

The x3-term PAL spectrum of the pelletized PVP-capped g-As$_2$Se$_3$ nanocomposite (i.e. wet-MM g-As$_2$Se$_3$) differ essentially demonstrating obvious changes in positron- and Ps-related annihilation channels, the corresponding changes in third and second component intensities (I_2 and I_3) being enhanced evidently (Table 1). As a consequence, the average lifetime $\tau_{av.}$ in this composite grows to 0.386 ns, while the τ_3 lifetime drops to 1.891 ns, tending towards Ps-related lifetime in pure PVP matrix (τ_3=1.867 ns) [22]. Hence, the Ps-decaying occurs rather in PVP environment than in "pure" g-As-Se matrix, this process being nearly three-times enhanced in respect to f_v=0.83% (see Table 2). In contrast, the defect-specific τ_2 lifetime grows abnormally in g-As$_2$Se$_3$/PVP nanocomposite approaching ~0.43 ns, which can be ascribed to positron trapping in large free-volume defects such as multi-vacancy clusters [17-19].

To identify free-volume nanostructurization in the pelletized g-As$_2$Se$_3$/PVP nanocomposite, the PAL spectrum of pelletized dry-milled g-As$_2$Se$_3$ is considered in respect to wet-milled one using the x3-x2-CDA [13] (Table 3).

TABLE 3. x3-x2-CDA trapping modes in dry-MM g-As$_2$Se$_3$ defined in respect to g-As$_2$Se$_3$/PVP nanocomposite.

First component			Second component			Positron trapping modes				
τ_n	I_n	$(\tau_n \cdot I_n)$	τ_{int}	I_{int}	$(\tau_{int} \cdot I_{int})$	τ_{av}^{NP}	τ_b^{NP}	κ_d^{NP}	$\tau_{int}-\tau_b^{NP}$	τ_{int}/τ_b^{NP}
ns	a.u.	ns	ns	a.u.	ns	ns	ns	ns^{-1}	ns	a.u.
0.194	0.334	0.065	0.352	0.472	0.166	0.287	0.263	1.35	0.09	1.34

The positive first and second component intensities (I_n and I_{int}) in the PAL spectrum reconstructed in terms of x3-x2-CDA, along with well-filled ($\tau_n \cdot I_n$) and ($\tau_{int} \cdot I_{int}$) component inputs testify that Ps-decaying sites in pelletized PVP-g-As$_2$Se$_3$ nanocomposite are transformed to positron-trapping sites in dry-MM g-As$_2$Se$_3$ pellets. The defect-related lifetime τ_{int}=0.352 ns shows the appeared positron traps represent interfacial voids, which are close in their free volumes to di- and/or tri-atomic vacancies in g-As-Se matrix, reaching ~0.25-0.28 nm in a radius (in a spherical approximation) as it follows from known semiempirical relationships for arsenic triselenide As$_3$Se$_3$ [17-19]. This finding agrees well with ($\tau_{int}-\tau_b^{NP}$)=0.09 ns and τ_{int}/τ_b^{NP}=1.34 values as character indicatives of these vacancies [12]. In dry-MM g-As$_2$Se$_3$ pellet, this positron-trapping channel substitutes the Ps-decaying contribution originated from inter-NPs holes with τ_3=2.087 ns by input from PVP-filled inter-NPs Ps-traps with τ_3=1.891 ns lifetime (Table 1). The whole trapping-conversion process, i.e. appearance of positron traps with defect-related lifetime τ_{int}=0.352 ns instead of Ps-decaying sites with τ_3=2.087 ns lifetime, occurs in a chemical environment possessing defect-free bulk positron lifetime τ_b^{NP}=0.263 ns (Table 3). This value is evidently above bulk positron lifetime in crystalline c-As$_2$Se$_3$ (τ_b=0.240 ns) [17], but below this lifetime in g-As$_2$Se$_3$ (τ_b=0.280-0.285 ns) as defined within STM from constrained-free x2-term decomposed PAL spectra, i.e. ignoring any competitive contribution from Ps-decaying channel [19]. Thus, the chemical environment of Ps-to-positron trapping conversion, i.e. inner spaces where positron traps appear (dry-MM g-As$_2$Se$_3$) instead of PVP-filled inter-NPs Ps-decay sites (wet-MM g-As$_2$Se$_3$), is indeed g-As-Se matrix.

In our consideratio, we have been grounded on assumption that Ps-to-positron trapping conversion is alone process linking dry-MM and wet-MM g-As$_2$Se$_3$. This condition seems to be really satisfied under small amount of PVP in nanocomposite due to the same positron annihilation channel from defect-free bulky states in both arsenicals.

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