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PAL spectroscopy of rare-earth doped Ga-Ge-Te/Se glasses

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Abstract

Positron annihilation lifetime (PAL) spectroscopy was applied for the first time to study free-volume void evolution in chalcogenide glasses of Ga-Ge-Te/Se cut-section exemplified by glassy Ga₁₀Ge₁₅Te₇₅ and Ga₁₀Ge₁₅Te₇₂Se₃ doped with 500 ppm of Tb³⁺ or Pr³⁺. The collected PAL spectra reconstructed within two-state trapping model reveal decaying tendency in positron trapping efficiency in these glasses under rare-earth doping. This effect results in unchanged or slightly increased defect-related lifetimes τ_2 at the cost of more strong decrease in I_2 intensities, as well as reduced positron trapping rate in defects and fraction of trapped positrons. Observed changes are ascribed to rare-earth activated elimination of intrinsic free volumes associated mainly with negatively-charged states of chalcogen atoms especially those neighboring with Ga-based polyhedrons.

Keywords: chalcogenides; glasses, positron annihilation spectroscopy, defects, microstructure

Introduction

Chalcogenide glasses (ChG), e.g. chemical compounds of chalcogens (S, Se or Te, but not O) with some elements from IV-V groups of the Periodic table quenched from a melt state, have found widespread application in modern *chalcogenide photonics* [1] because of their superior transmittance in IR spectral region including both atmospheric (3-5 μm and 8-12 μm) and space telecommunication windows [2-4]. In general, this remarkable feature is caused by high-phonon frequencies typical for chalcogenide-like environment essentially overcome those in oxide media. This functionality can be further stretched by doping ChG with some rare-earth (RE) activators like Pr³⁺, Tb³⁺, Dy³⁺, Er³⁺, etc., which possess numerous radiative transitions emitting in near and mid-IR range up to 10 μm thus providing advanced optical fibers for this spectral domain [5-7]. However, because of very low solubility in chalcogenide compounds [8-9], the ChG should be essentially modified to accommodate

RE ions in electrically active functional state allowing light generation. As a rule, it can be achieved only in ChG modified by such codopants as Ga or In, which possess unique ability of charge compensation for *guest* RE ions embedded in *host* ChG matrix [5,8-12]. In fact, this effect is realized owing to complicated structural changes, stretching over both *atomic-specific* and *atomic-deficient levels*, where intrinsic free-volume elements of low-electron densities (vacancies and vacancy-like clusters, their agglomerates, voids, etc.) play an important role [13-15].

This work is aimed to recognize how these structural changes in RE-doped ChG possessing a relatively high content of Ga additions will be accessible (if any) for positron annihilation lifetime (PAL) spectroscopy, a high-informative tool successfully applied recently to identify sub-atomistic free volumes in many glass-forming media [15-19].

Experimental

Two Ga-contained ChG of Ga-Ge-Te/Se cut-section doped with 500 ppm of Tb^{3+} were tested with PAL spectroscopy, they being $Ga_{10}Ge_{15}Te_{75}$ (one of most stable glassy alloy in Ga-Ge-Te system [20]) and $Ga_{10}Ge_{15}Te_{72}Se_3$, where some amount of Se was introduced instead of Te to form glassy alloy more stable against crystallization [21]. In the latter case, we also used the Pr^{3+} ions as doping agents in the same content (500 ppm). The glassy samples were prepared by conventional melt-quenching route using high-purity commercial elemental precursors Ga (7N), Se (5N), Te (6N), Ge (5N), Pr_2Se_3 (3N) and Tb_2Se_3 (3N). The appropriate amounts of initial elements with total weight of 25-30 g were inserted into a silica tube of 10 mm in a diameter. The ampoules were sealed under a vacuum and heated to 950°C in a rocking furnace for 1 h, after they were cooled down to 900°C for 10 h homogenization followed by quenching into room-temperature water from 700°C. To remove mechanical strains caused by rapid quenching, the ChG samples were annealed during 5 h at 10°C below glass transition temperature. The obtained rods were cut into disks of ~2 mm in thickness and polished to a high optical quality.

The prepared ChG samples were in a glassy form as it followed from absence of any sharp crystalline peaks in X-ray diffraction (XRD) patterns demonstrating only stretched amorphous halos and characteristic coinchoidal fracture on fresh cut-sections. No significant changes between optical properties of un-doped and RE-doped ChG were observed, apart from slight long-wave shift in optical transmission edge due to RE absorption close to 2 μm and absorption bands of Tb^{3+} at 2.95 and 4.75 μm (transitions from ground 7F_6 state to 7F_4 and 7F_5 levels, respectively) and Pr^{3+} at 2.05 and 4.50 μm (transitions from ground 3H_4 state to 3F_2 and 3H_5 levels, respectively) [9].

The 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 (an ambient temperature of 22°C and relative humidity of 35 %). The pairs of identical plane-parallel samples of each composition in typical *sandwich* geometry (covering ^{22}Na isotope of slow ~50 kBq activity) were

employed, the contribution from a source being taken at the level of 12 % ($\tau=0.352$ ns). To ensure reliable PAL data, three independent measuring cycles each covering nearly 1 M elementary positron annihilation events were performed. The experimental results were fitted by two single exponents under normalized intensities ($I_1 + I_2 = 1$) using LT 9.0 program [22]. Introducing third component to fitting curve did not improve decomposition goodness significantly, the estimated input from this long-lived component in the PAL spectra being less than 1 %. Fitting uncertainties in positron lifetimes $\tau_{1,2}$ and component intensities $I_{1,2}$ were at the level of $\pm(0.0020-0.0040)$ ns and $\pm(0.0030-0.0050)$, respectively. This provides a reliable final error-bar for such *ex-situ* measuring protocol not worse than ± 0.005 ns in lifetimes $\tau_{1,2}$ and ± 0.5 % in intensities $I_{1,2}$. Mathematical formalism of known two-state trapping model with only one kind of positron traps [23-27] was utilized to parameterize mean τ_{av} and defect-free bulk τ_b lifetimes, as well as trapping rate in defects κ_d . The difference between defect-related $\tau_d=\tau_2$ and bulk positron lifetimes ($\tau_2-\tau_b$) was taken as a signature of size of positron traps in terms of equivalent number of vacancies, while τ_2/τ_b ratio was ascribed to the nature of these defects [23]. The fraction of trapped positrons $\eta=\tau_1\cdot\kappa_d$ participating in an annihilation was also controlled.

Results and Discussion

The typical raw PAL spectra of the studied glassy $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ samples, both un-doped and Tb^{3+} -doped ones, reconstructed from two-component fitting at the general background of standard source contribution are shown in Fig. 1a and 1b, respectively (the similar spectra were collected for other glassy alloys). These PAL spectra as typical histograms of elementary positron annihilation events are characterized by narrow peaks and regions of long fluent decaying of coincidence counts in a time. The limited values of statistical scatter of variance compactly grouped around 0-axis testify that PAL measurements were adequately described by this fitting procedure. Thus, the decaying behavior of such curve can be represented by sum of separate exponents with different time constants inversed to positron lifetimes [23-25].

The best-fit positron trapping parameters of the studied ChG calculated within two-state model [23-27] are given in Table 1. The parent $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ glass is characterized by quite high defect-related positron lifetime $\tau_2=0.365$ ns and moderate intensity $I_2=0.43$ reflecting positron trapping in relatively stretched free-volume defects such as multiatomic vacancy clusters [28]. With 3 at. % of Se substituted Te to produce $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ glass, the positron trapping attains features character for more fragmented void structure [27]. The τ_2 lifetime slightly decreases to 0.346 ns, while I_2 intensity shows more noticeable growing tendency to 0.52, thus resulting in more than five-times enhanced trapping rate in free-volume defects in $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ glass.

It is evidently seen from Fig. 1 that RE doping does not change essentially mass-center position of all positron annihilation events τ_{av} , as well as characteristic non-defect bulk positron lifetimes τ_b of both $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ ChG, since all changes are within statistical error-bar of

positron lifetimes determination (see Table 1). Under a such condition, the physically realistic meaning attains only second component in the reconstructed PAL spectrum, the corresponding τ_2 lifetime reflecting low-electron density volumes where positrons are trapped and I_2 intensity being proportional to concentration of these traps [23]. The defect-related positron lifetime τ_2 does not change with Tb^{3+} doping in $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ ChG ($\tau_2=0.365$ ns), but rather only slightly grows in partially Se-substituted glassy $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ alloy (Table 1). The most essential growing effect in τ_2 lifetime from 0.346 ns to 0.356 ns is also caused in this $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ ChG affected by Pr^{3+} additions. At the same time, the RE doping is accompanied by considerable decrease in the I_2 intensity in both glassy $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$, this effect reaching as high as 6 % in case of Tb^{3+} -doped $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ glass.

Thus, the observed changes in the fitting parameters describing the reconstructed PAL-spectra correspond to obvious decaying tendency in positron trapping efficiency in the studied ChG under RE doping. This effect results in the reduction of trapping rate in defects κ_d and fraction of trapped positrons η (Table 1). Let's clarify physical meaning of this process and give its possible explanation in terms of known microstructure models developed for positron trapping in ChG [17,28-34].

It is known that positrons are captured in the ChG by extended free-volume defects localized in a vicinity of chalcogen (Ch) atoms [17,29-31]. Such positron traps are formed by *atomic-accessible cores* of geometrical free volumes surrounded by *atomic-inaccessible shell* of overlapped bond-free solid angles (BFSA), e.g. low-electron density spaces appeared due to directionality of covalent chemical bonds around Ch atoms in a glassy network [35]. In homoatomic ChG like Se or Ch-rich As/Ge-Se/Te glasses, the neutral Ch_2^0 states (the sub- and super-script stays for local coordination and electrical charge, respectively) are mostly dominant in the overall balance of positron trapping events, since As/Ge-related traps are rather ineffective in view of their repulsive potential to positrons [31]. However, in heteroatomic ChG like glassy As/Ge-Ch alloys close to stoichiometry, the positron trapping prevails on free-volume defects surrounded by overlapped BFSA, which are localized in the bottom of main glass-forming structural units (trigonal $\text{AsCh}_{3/2}$ pyramids and tetragonal $\text{GeCh}_{4/2}$ tetrahedrons). Because of significant difference in the electronegativity of *anion-type* Ch and *cation-type* As/Ge atoms [36], such defects related to local Ch_2^- configurations can be imagined as prototypes of *negatively-charged vacancies* like *cation vacancies* in crystalline counterparts of these compounds [23,37]. Correspondingly, the defect-related positron annihilation lifetimes $\tau_d=\tau_2$ grow with going from glassy Se (with positron traps having preferential neutral Ch_2^0 -type shell within homoatomic chain- and ring-like configurations) to stoichiometric As_2Ch_3 (with positron traps having preferential Ch_2^- -type shell in the bottom of $\text{AsCh}_{3/2}$ pyramids or $\text{GeCh}_{4/2}$ tetrahedrons), showing an obvious anomaly in respect to compositional trend in a molar volume, as it was proved experimentally [31].

To be functional in ChG, the RE dopants should occupy an active “3+” state (Tb^{3+} or Pr^{3+}). Under a condition of global electroneutrality proper to full saturation of covalent bonding in ChG networks (in respect to known 8-*N* rule [38]), this demands local inhomogeneities possessing an

effective negative charge to compensate an excess of positive electrical charge of embedded RE ions. Such inhomogeneities can be produced owing to incorporation of Ga (or alternatively In) in ChG without disturbing their glass-forming ability [8,9]. As typical metallic atoms, the Ga dopants tend to saturate their highest local coordination in respect to Ch-environment (predominantly tetrahedral coordination in glassy Ga-Ge-Te system [10,11,39-41], obviously overcoming a full saturation of covalent chemical bonding of un-doped ChG matrix [8]. Thus, some Ch atoms occur to be poorly linked with Ga (approaching Ch^{2-} state), ensuring an excess of compensating negative charge for embedded RE ions. In other words, to satisfy a condition of global charge compensation within a whole glassy matrix, the positively charged RE ions act as *charge-balancing cations* in respect to negatively charged Ch ions linked with Ga additions.

Thus, a complicated network of cycle-type formations built of Ge- and Ga-based polyhedrons (tetrahedra) showing a character topology of atomic-deficient free-volume voids is stabilized in glassy $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$. Under a random distribution and high enough content (10 mol. %), the Ga-based tetrahedra contribute to a majority of such voids, thus enhancing positron trapping efficiency in these ChG. However, because of overall negative charge, just these free-volume voids are also effective attractors for RE dopants. So under RE doping, these voids occupied by Tb^{3+} and Pr^{3+} ions (through Ga-Te-RE linkages [8]) are subsequently eliminated as potential positron trapping sites. Therefore, in all cases of RE doping, the intensities of defect-related component I_2 in the reconstructed PAL spectra are sharply inhibited (see Table 1). Since all free-volume voids accommodated Ga-based tetrahedrons equally participate in this process, there are no essential shift in the averaged values of defect-related positron lifetimes τ_2 , which is in good harmony with our experimental data in Table 1.

Conclusions

The PAL spectroscopy was applied to study free-volume void evolution in glassy $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ and $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{72}\text{Se}_3$ alloys affected by doping with 500 ppm of Tb^{3+} or Pr^{3+} ions. Within two-state positron trapping model, the principal effect of doping is revealed as conserving and slight increase in defect-related positron lifetimes τ_2 at the cost of essentially reduced I_2 intensities. The corresponding changes in positron trapping modes extracted from two-component reconstructed experimental PAL spectra are ascribed to RE activated elimination of intrinsic free-volume voids associated mainly with negatively-charged states of chalcogen atoms neighboring with Ga-based polyhedrons.

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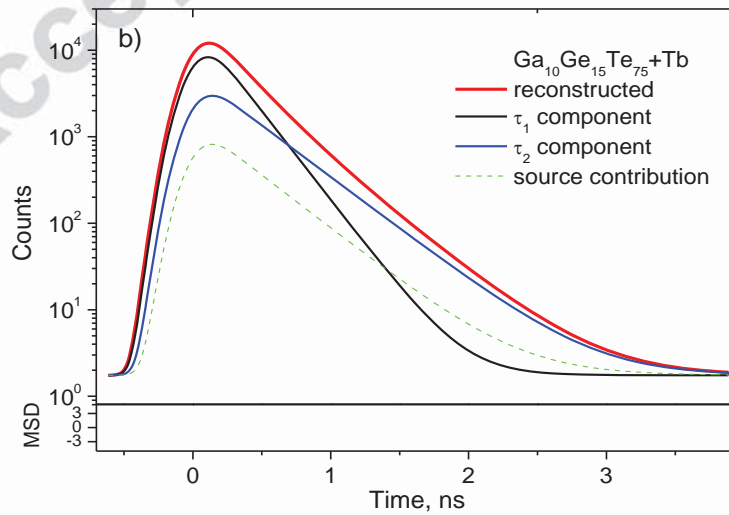
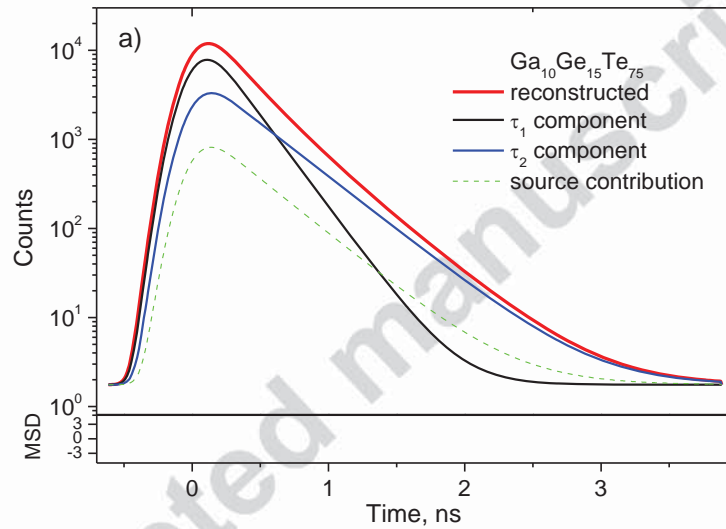
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Table 1. Fitting parameters and positron trapping modes describing two-component reconstructed PAL spectra of RE-doped ChG alloys

Glass composition, RE doping ions	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
	ns	ns	a.u.	ns	ns	ns ⁻¹	ns	-	-
Ga ₁₀ Ge ₁₅ Te ₇₅	0.211	0.365	0.431	0.277	0.258	0.86	0.11	1.41	0.18
Ga ₁₀ Ge ₁₅ Te ₇₅ + 500 ppm Tb	0.207	0.364	0.401	0.270	0.251	0.83	0.11	1.45	0.17
Ga ₁₀ Ge ₁₅ Te ₇₂ Se ₃	0.197	0.346	0.520	0.275	0.254	1.13	0.09	1.36	0.22
Ga ₁₀ Ge ₁₅ Te ₇₂ Se ₃ + 500 ppm Tb	0.200	0.350	0.463	0.270	0.250	0.99	0.10	1.40	0.20
Ga ₁₀ Ge ₁₅ Te ₇₂ Se ₃ + 500 ppm Pr	0.203	0.356	0.481	0.277	0.256	1.02	0.10	1.39	0.21



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Fig. 1. Raw PAL spectra of ChG reconstructed from two-component fitting at the general background of source contribution: a – $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$; b – $\text{Ga}_{10}\text{Ge}_{15}\text{Te}_{75}$ doped with 500 ppm of Tb^{3+} (bottom inset shows statistical scatter of variance).

Highlights:

Positron annihilation spectroscopy to study rare-earth doping in Ga-Ge-Te/Se glasses
Two-state trapping model to reconstruct experimental positron lifetime spectra
Decaying tendency in positron trapping efficiency in glasses under rare-earth doping
Rare-earth activated elimination of free-volume voids associated with Ga-tetrahedrons

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