

Transformation of Nanostructured Voids in the Crystallized $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ Glasses

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Abstract—Transformation of voids in crystallized $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$, $x = 0; 5; 10; 15$ chalcogenide glasses was studied by positron annihilation lifetime spectroscopy. The CsCl content in $\text{GeS}_2\text{-Ga}_2\text{S}_3$ glassy matrix changed the defect-related component in positron lifetime spectra and confirmed the structural void agglomeration in comparison with the base glass. A larger amount of CsCl in $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{85}(\text{CsCl})_{15}$ glass resulted in void fragmentation due to loosening of the structure.

Index Terms—Nanostructures; glasses; crystallization; positron trapping; positronium decay

I. INTRODUCTION

Sulfide-based chalcogenide glasses (ChG) are considered as good candidates for optoelectronics and photonics applications due to a wide optical transmission range (from 0.45 to 12 μm) [1-3]. It was shown that alkali halides like CsCl, added into $\text{GeS}_2\text{-Ga}_2\text{S}_3$ glassy matrix, expanded the visible transmission window towards shorter wavelengths [4,5]. Moreover, thermal, mechanical and physical properties of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ glasses can be improved by a controlled crystallization during heat treatment [6,7]. Such processes lead to a nanostructural transformation of internal free-volume voids in crystallized $\text{GeS}_2\text{-Ga}_2\text{S}_3$ chalcogenide glasses with different CsCl content.

There are many experimental techniques to study the atomic void structure of solids [8-11], but they are limited at the sub-nanometer scale. One of the informative tools used to identify and study internal free volumes in various materials is positron annihilation lifetime (PAL) spectroscopy [12,13]. This method is based on the positron-electron interaction in condensed matter [14]. In chalcogenide glasses and glass-ceramics, PAL spectroscopy is used to study voids in the frame of the model that considers two channels – positron trapping in extended free-volume defects and ortho-positronium (o-Ps) decaying in holes [13]. In addition, PAL measurements are effective for the study of atomic void structure in solids affected by different nanostructured elements (nucleates, agglomerates, fragments of crystallites, vacancy clusters and free-volume voids, etc.) [14].

In previous works [15,16], we investigated the free-volume structure in $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ chalcogenide glass with controlled crystallization, after thermal annealing above glass transition temperature over different time frames. We also analyzed interface void volumes formed by nanocrystals using the x3-x2-decomposition procedure described in Ref. [16]. Transformations of the defect-related component of the PAL lifetime spectra for crystallized $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ chalcogenide glass confirmed the structural fragmentation of larger voids into smaller ones at the crystallization of GeGa_4Se , Ga_2Se_3 and GeSe_2 phases with further void agglomeration during the initial stage of annealing [15]. In the case of as-prepared $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ glasses, the free-volume void agglomeration is observed with increasing CsCl content in the glassy matrix. In this work, we analyzed the free-volume nanostructural evolution in $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$, $x = 0; 5; 10; 15$ glasses caused by completely “cold” crystallization using PAL spectroscopy. Simultaneous positron-positronium trapping (x3-x2-decomposition) as proposed earlier is considered in order to analyze the free-volume nanostructured media formed by CsCl.

II. EXPERIMENTAL

$\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ chalcogenide glasses were prepared from a mixture of high purity materials (99.999 % for Ge, Ga, S and 99.9 % for CsCl) in a silica ampule kept at 10^{-6} Pa vacuum as described in detail elsewhere [5,7]. The raw materials were melted at 850 °C in a silica tube for several hours. After melting, glasses were annealed at 15 °C, *i.e.* below the glass transition temperature T_g for each glass [5] in order to minimize inner strains. The crystallization of $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$, $x = 0; 5; 10; 15$ glasses was performed by thermal treatment at $(T_g + 30)$ °C. This temperature results in a full crystallization of chalcogenide glasses, allowing the growth of nanoparticles inside the glassy matrix.

The PAL spectra were measured with an ORTEC system with a resolution of 230 ps at $T = 22$ °C and relative humidity of $RH = 35$ % (see Refs. [16-18] for additional details). The

^{22}Na isotope was used as positron source. Two identical samples were placed on the positron source in a "sandwich" configuration. Each PAL spectrum was investigated with a number of channels of 8000.

The measured PAL spectra were processed using version 9.0 of the LT software [19] and processed by applying three-component fitting procedure, with lifetimes τ_1 , τ_2 , τ_3 and intensities I_1 , I_2 , I_3 being principal parameters. The positron trapping modes (average positron lifetimes τ_{av} , positron lifetime in defect-free bulk τ_b and positron trapping rate in defects κ_d) were calculated using the well-known two-state positron trapping model [20,21]. In addition, the $(\tau_2 - \tau_b)$ difference, describing the size of extended free-volume defects, where positrons are trapped, and the τ_2/τ_b ratio were correlated with the nature of these defects.

To describe the formation of nanostructures in $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ glasses caused by the content of CsCl and full crystallization, the x3-x2-decomposition algorithm was used as a test-indicator in terms of the transformation of o-Ps-sites in the undoped matrix towards positron-trapping sites in a CsCl-doped and nanoparticle-modified glass according to [16].

III. RESULTS AND DISCUSSION

As shown earlier in [15,16], "cold" crystallization in chalcogenide glasses leads to transformations of their atomic void structure. The fitting parameters and positron trapping modes obtained within three-component procedure for PAL spectra of $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$, $x = 0; 5; 10; 15$ glasses are given in Fig. 1, Fig. 2 and Fig. 3, respectively. The first component (see Fig. 1) with the fitting parameters τ_1 and I_1 has no physical meaning which is also true for other chalcogenide glasses [15].

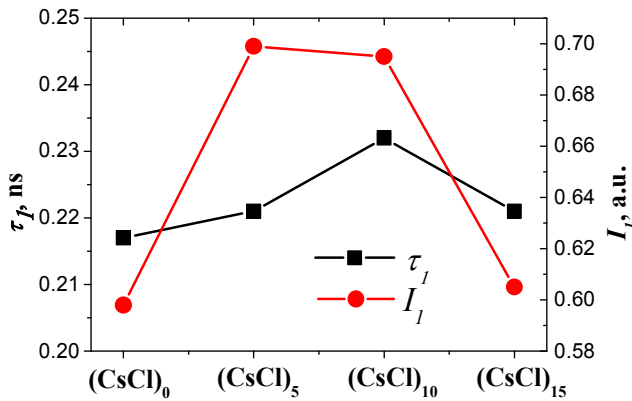


Fig. 1. Lifetime τ_1 and intensity I_1 as a function of CsCl content in $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ glass.

The τ_2 lifetime reflects the size of free voids where positrons are trapped, and the intensity I_2 is proportional to the number of these voids if the defect-free bulk annihilation lifetime is the same [22]. The third component with the lifetime τ_3 and the intensity I_3 is obtained by the fitting procedure, confirming the o-Ps formation at a level of 1-2%. We will now

focus on analyzing the second (τ_2 , I_2) component which represents the main nanostructural free-volume void transformation in crystallized $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ chalcogenide glasses with different amounts of CsCl in the glass matrix.

With the increase of $(\text{CsCl})_x$ additives to $x=5$ and $x=10$, the lifetime τ_2 increases and intensity I_2 decreases as compared to $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ (see Fig. 2). These transformations correspond to void expansion and agglomeration (see Fig. 3) as well as in $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-CsCl}$ chalcogenide glasses before crystallization [23].

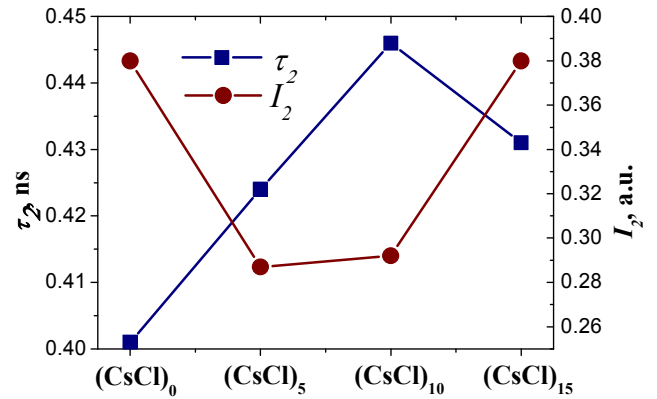


Fig. 2. Lifetime τ_2 and intensity I_2 as a function of CsCl content in $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ glass.

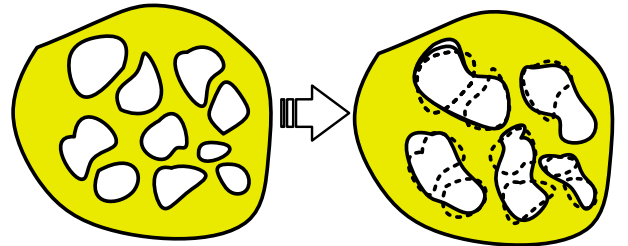


Fig. 3. Schematic illustration of void agglomeration in Ge-Ga-S-CsCl glasses.

Eventually, the positron trapping rate κ_d in voids reduces mainly due to the increase of the intensity I_2 . Other positron trapping parameters such as the lifetime τ_b and the difference $(\tau_2 - \tau_b)$, reflecting the size of extended free-volume defects where positrons are trapped, are in correlation with these changes (Fig. 4 and Fig. 5). The τ_2/τ_b ratio shows a very small change with CsCl content (Fig. 5).

Another tendency is observed for crystallized $(80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3)_{85}(\text{CsCl})_{15}$ glass in comparison with other CsCl-containing chalcogenide glasses. The lifetime τ_2 increases and the intensity I_2 is stable with respect to $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ glasses indicating slow void expansion in chalcogenide glasses with CsCl additives (Fig. 2).

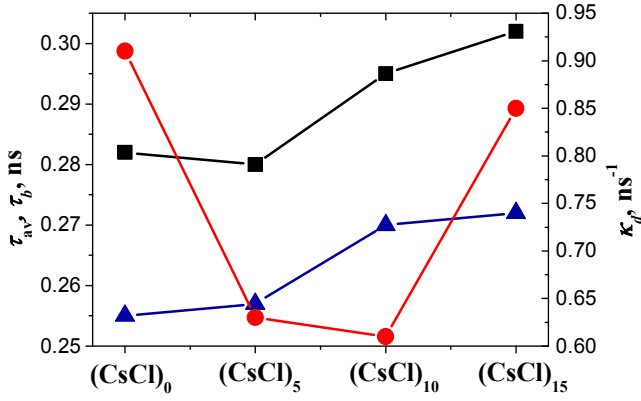


Fig. 4. Average lifetime, defect-free lifetime and positron trapping rate in defects as a function of CsCl content in 80GeS₂-20Ga₂S₃ glass describing void agglomeration.

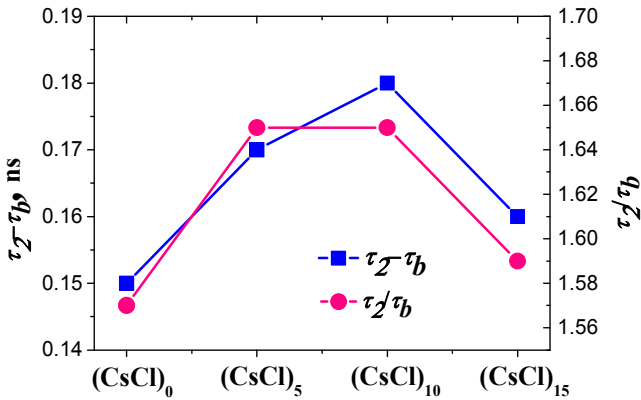


Fig. 5. Size of extended free-volume defects, where positrons are trapped, τ_2/τ_b ratio as a function of CsCl content in 80GeS₂-20Ga₂S₃ glass.

However, as compared to (80GeS₂-20Ga₂S₃)₉₀(CsCl)₁₀ glasses, in (80GeS₂-20Ga₂S₃)₈₅(CsCl)₁₅ chalcogenide glass the lifetime τ_2 decreases and the intensity I_2 increases, proving a possible void fragmentation [15]. Such a free-volume transformation is caused by loosening of inner glass structure when CsCl content is high.

To study the free-volume void transformation processes caused by the formation of nanostructures in CsCl-containing Ge-Ga-S chalcogenide glasses, where inner inclusions affect both positron and Ps trapping, the x3-x2-decomposition algorithm was used [16]. To do this, the PAL spectra of 80GeS₂-20Ga₂S₃ chalcogenide glass and of glasses with CsCl additives were processed using three-component x3 fitting. It is shown that the o-Ps decaying plays no essential role in the formation of nanostructures as the intensity is within the standard deviation error. The lifetime τ_3 slightly rises in crystallized samples with CsCl (see Fig. 6).

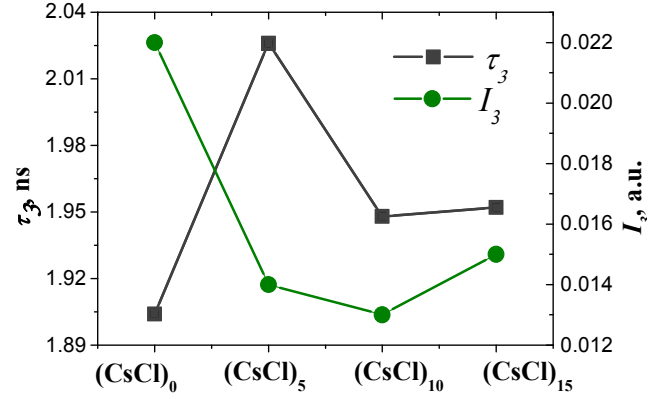


Fig. 6. Lifetime τ_3 and intensity I_3 as a function of CsCl content in 80GeS₂-20Ga₂S₃ glass.

As far as mixed positron- and o-Ps-trapping modes are considered, all samples show almost the same average lifetime τ_{av} . Large values of the lifetime τ_b (0.26-0.27 ns) demonstrate a rather loose packing of nanoparticles formed after crystallization which is caused by impossibility to distinguish inputs from positron- and o-Ps-trapping modes. So-called "pure" positron-positronium modes calculated using x3-x2-decomposition formalism described in [16] can be extracted from the full trapping processes data (Table 1). The components (τ_n, I_n) and (τ_{int}, I_{int}) describe physical parametrization of nanoparticle-connected sites in crystallized glasses within the two-term decomposed PAL spectrum. The defect-related lifetime τ_{int} reflects positron trapping sites due to embedded CsCl and nanoparticles were formed after the crystallization.

The increase of the lifetime τ_{int} and the intensity I_{int} in the recalculated final x2-spectrum for (80GeS₂-20Ga₂S₃)₉₅(CsCl)₅ and (80GeS₂-20Ga₂S₃)₉₀(CsCl)₁₀ glasses with respect to (80GeS₂-20Ga₂S₃)₁₀₀(CsCl)₀ glass indicate that realistic process is very likely connected with the expansion of voids formed as a consequence of CsCl addition and full crystallization into inner structure of glasses.

Recalculating these results with respect to (80GeS₂-20Ga₂S₃)₉₅(CsCl)₅ glass (the second line in Table 3), one can observe two different tendencies in the void transformation. The CsCl additive forms new free volume voids (new positron-trapping sites appear) in (80GeS₂-20Ga₂S₃)₉₅(CsCl)₅ glass in comparison with the base 80GeS₂-20Ga₂S₃ chalcogenide glass.

Crystallized (80GeS₂-20Ga₂S₃)₉₀(CsCl)₁₀ glass is affected by void agglomeration, while in (80GeS₂-20Ga₂S₃)₈₅(CsCl)₁₅ glass, void fragmentation occurs. The bulk positron lifetime in all samples corresponds to positron trapping occurring in nanocrystalline particles. Interlace voids are not very large because the characteristic value of 0.27-0.30 ns can be connected with typical free volumes of mono- and divacancies [15,16, 23].

TABLE 1. PAL TRAPPING PARAMETERS FOR CRYSTALLIZED $(80\text{GeS}_2-20\text{Ga}_2\text{S}_3)_{100-x}(\text{CsCl})_x$, $x = 0; 5; 10; 15$ GLASSES PROCESSED WITH THE X3-X2-DECOMPOSITION ALGORITHM (WITH RESPECT TO THE ORIGINAL MATRIX WITHOUT CsCl)

Sample	τ_{ns} ns	τ_{ints} ns	I_{ints} a.u.	τ_b ns	κ_{I_s} ns^{-1}	τ_{ns} ns	τ_{ints} ns	I_{ints} a.u.	τ_b ns	κ_{I_s} ns^{-1}
(CsCl) ₀	-	-	-	-	-	0,237	0.547	-0.071	0.293	0.812
(CsCl) ₅	0,237	0.547	0.045	0.277	0.611	-	-	-	-	-
(CsCl) ₁₀	0,237	0.596	0.067	0.320	0.536	0.345	0.676	0.026	0.403	0.415
(CsCl) ₁₅	0,228	0.495	0.121	0.284	0.854	0.222	0.461	0.073	0.276	0.867

CONCLUSIONS

The transformation of intrinsic free-volume voids in fully crystallized $80\text{GeS}_2-20\text{Ga}_2\text{S}_3$ chalcogenide glasses caused by the addition of CsCl leads to a specific void agglomeration in comparison with the base glass and to the expansion of voids with increasing of CsCl amount. In comparison with $(80\text{GeS}_2-20\text{Ga}_2\text{S}_3)_{90}(\text{CsCl})_{10}$ glass, in $(80\text{GeS}_2-20\text{Ga}_2\text{S}_3)_{85}(\text{CsCl})_{15}$ chalcogenide glass the void fragmentation is possible due to loosening of the glass structure. Using the x3-x2-decomposition algorithm it was shown that CsCl additive forms new interface voids (positron-trapping sites) in $\text{GeS}_2-\text{Ga}_2\text{S}_3$ matrix and stimulates their expansion in crystallized glassy matrix.

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