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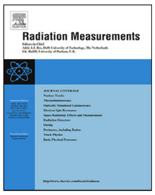

Positron trapping defects in free-volume investigation of Ge–Ga–S–CsCl glasses

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HIGHLIGHTS

- CsCl additives in Ge–Ga–S glassy matrix lead to the agglomeration of voids.
- Full crystallization of Ge–Ga–S–CsCl glasses corresponds to the formation of defect voids.
- Gamma-irradiation of glass stimulates the creation of additional defects and darkening.

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ABSTRACT

Evolution of free-volume positron trapping defects caused by crystallization process in $(80GeS_2-20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \leq x \leq 15$ chalcogenide-chalcohalide glasses was studied by positron annihilation lifetime technique. It is established that CsCl additives in Ge–Ga–S glassy matrix transform defect-related component spectra, indicating that the agglomeration of free-volume voids occurs in initial and crystallized $(80GeS_2-20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \leq x \leq 10$ glasses. Void fragmentation in $(80GeS_2-20Ga_2S_3)_{85}(CsCl)_{15}$ glass can be associated with loosing of their inner structure. Full crystallization in each of these glasses corresponds to the formation of defect-related voids. These trends are confirmed by positron-positronium decomposition algorithm. It is shown, that CsCl additives result in white shift in the visible regions in transmission spectra. The γ-irradiation of $80GeS_2-20Ga_2S_3$ base glass leads to slight long-wavelength shift of the fundamental optical absorption edge and decreasing of transmission speaks in favor of possible formation of additional defects in glasses and their darkening.

1. Introduction

Chalcogenide glass (ChG) materials with improved exploitation properties are important for novel applications (Ailavajhala et al., 2014; Petit et al., 2008; Richardson et al., 2010). Unique multifunctionality of $GeS_2-Ga_2S_3$ ChG family manifests in luminescence phenomena, *e.g.* intense radioactive photoemission of rear-earth doping additives introduced in modified ChG (Kostka et al., 2015; Zhang et al., 2014; Seddon et al., 2010), ion-conductive phenomena, *e.g.* abnormal conductivity of Li^+ ions in solid electrolytes (Ren et al., 2011) and diffusive-related phenomena, *e.g.* reversible self-healing effects observed in photoinduced refraction owing to ion-conducting additives (Yao and Martin, 2008).

In all the above cases, only optimized defect inner-pore structure of basic $GeS_2-Ga_2S_3$ ChG defines their final glassy-like state – its extended functionality connected with the possibility to accommodate outer atoms and their groups. It is of high importance that by controlled halide (CsCl) addition these ChG can be easily transformed in chalcogenide ceramics transparent in IR region, as it was well demonstrated in (Yao and Martin, 2008). In addition, the compositional series of ChG can range from model binary (GeS_2, As_2S_3) to ecologically-friendly Ga-doped quasi-binary $GeS_2-Ga_2S_3$ systems as host matrix for rear-earth activators, and then modified with alkali halides MX (M = Cs, X = Cl) (Calvez et al.,

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2007) to ensure functionality in visible range and activated by rear-earth ions (Dy^{3+} or Pr^{3+}) to produce highly-efficient photonics media (Lu et al., 2014).

However, the functionality mechanism of these systems is yet unknown because their free-volume defect-related structure has not been investigated, significantly limiting the further progress in modern IR photonics. It is well-known, that the nearest atomic arrangement in a glasses, ceramics and nanomaterials can be adequately studied with numerous experimental measuring methods (like vibration and Raman scattering spectroscopy, XRD, SEM, XPS, XAFS, XANES, NMR, etc.) (Purans et al., 1987; Majid et al., 1998; Karbovnyk et al., 2014; Bellucci et al., 2008; Balasubramanian et al., 2006; Bellucci et al., 2007; Popov et al., 2013). However, the choice of probes available to study atomic-deficient distribution is rather limited, especially at sub-nanometer scale. One of the best techniques capable to probe such finest free volumes is the positron annihilation lifetime (PAL) spectroscopy, a well-approved tool to study atomic void structure (nucleates, fragmentation, vacancy clusters, etc.) in binary ChG (Golovchak et al., 2013). In this work, we are analyzing free-volume defects and voids in as-prepared and crystallized nanostructurally modified mixed chalcohalide glassy compounds of ChG-MX type ($(80GeS_2{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 15$) using PAL technique. The x3-x2-decomposition algorithm proposed in (Shpotyuk et al., 2015) is used in this work to analyze free-volume nanostructured media caused by crystallization processes in the host $GeS_2{-}Ga_2S_3{-}CsCl$ matrix.

2. Experimental

$GeS_2{-}Ga_2S_3{-}CsCl$ glasses were prepared from Ge, Ga, S and CsCl materials in silica ampoule kept under 10^{-6} Pa vacuum, as described earlier in (Calvez et al., 2010; Shpotyuk et al., 2014). Materials were melted at 850 °C in a silica tube for several hours. The $(80GeS_2{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 15$ glasses were annealed at 15 °C below glass transition temperature T_g for all glasses (Masselin et al., 2012) to minimize inner strains. The crystallization of ChG was carried out at thermal annealing at ($T_g + 30$ °C). It was found that after such processing the complete crystallization of samples occurred.

The influence of γ-irradiation on optical properties of base $80GeS_2{-}20Ga_2S_3$ ChG was investigated using Co^{60} source. The dose of γ-irradiation was near 0.8 MGy, and the total duration of this procedure was 2 months.

Transformation of free-volume defects and voids in $(80GeS_2{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 15$ glasses was investigated by PAL method using ORTEC spectrometer (positron source – ^{60}Co isotope) at 22 °C and relative humidity of 35%. Each spectrum was measured for two identical samples with a channel width of 6.15 ps and analyzed using LT 9.0 computer program (Kansy, 1996).

In our previous work (Shpotyuk et al., 2015), we used a two-component fitting procedure to reconstruct the measured PAL spectra, this being achieved by corresponding choice of source contribution. The improved statistical treatment in this research for a majority of the studied samples testifies that three-component unconstrained fitting has an obvious preference in view of better approximation for PAL spectra. Thus, the best results were obtained using model of three components with lifetimes τ_1, τ_2, τ_3 and intensities I_1, I_2, I_3 reflecting positron and positronium (ortho-positronium trapping) parameters (Krause-Rehberg and Leipner, 1999; Jean et al., 2003). The first component with τ_1 and I_1 is of no physical meaning, positron trapping in free-volume entities and defects corresponds to the second component (τ_2, I_2). The third component (τ_3, I_3) in the envelope of the fitting curves corresponds to positronium formation. PAL experiment and peculiarities of mathematical treatment is described in details elsewhere (Golovchak et al., 2013; Shpotyuk et al., 2014; Klym et al., 2014; Filipecki et al., 2007).

Positron trapping parameters such as average positron lifetime $\tau_{av.}$, defect-free positron lifetime τ_b and positron trapping rate in defects κ_d were calculated using well-known positron-trapping model (Krause-Rehberg and Leipner, 1999; Alatalo et al., 1996). The $(\tau_2 - \tau_b)$ difference demonstrates size of free-volume defects where positrons are trapped, and the τ_2/τ_b ratio reflects the nature of these defects.

Nanostructurization of $GeS_2{-}Ga_2S_3{-}CsCl$ glasses due to full crystallization was characterized using the x3-x2-decomposition algorithm as an indicator of positron-positronium transformation in host and modified matrix. Methodological approach to the implementation of this algorithm was discussed in (Shpotyuk et al., 2015).

3. Results and discussion

As depicted in Fig. 1, the addition of CsCl results in white shift in the visible regions, in agreement with (Masselin et al., 2012). The transmission increases with CsCl concentration from 75% in $(CsCl)_0$–80% in $(CsCl)_{10}$ and $(CsCl)_{15}$. By adding up to 15% mol. of the alkali halide in the glassy matrix, the band-gap evolves from 2.64 eV to 2.91 eV. From a structural point of view, the addition of less than 15% of CsCl in $GeS_2{-}Ga_2S_3$ glasses is characterized by the formation of $GaS_{4-x}Cl_x$ tetrahedra that are dispersed in the glass network (Masselin et al., 2012). The average number of Ga–S bands decreases in favor of the average number of Ga–Cl bonds.

The slight long-wavelength shift of the fundamental optical absorption edge and the decrease in transmission are observed in glasses after γ-irradiation with dose near 0.8 MGy during 2 months (Fig. 2). This indicates possible formation of additional defects in $80GeS_2{-}20Ga_2S_3$ ChG and their darkening. In other worlds, after γ-irradiation, nanovoids with different size are created as intrinsic structural defects associated with topologically uncoordinated negative-changed centers. These defect centers form additional energy levels both near the bottom of the conduction band and in the vicinity of the valence band, as well as additional intrinsic electric fields. The mechanism of irradiation-induced darkening of $80GeS_2{-}20Ga_2S_3$ ChG is connected with oxidation processes most probably related with the appearance of GeS_2 phase at the surface of the glasses.

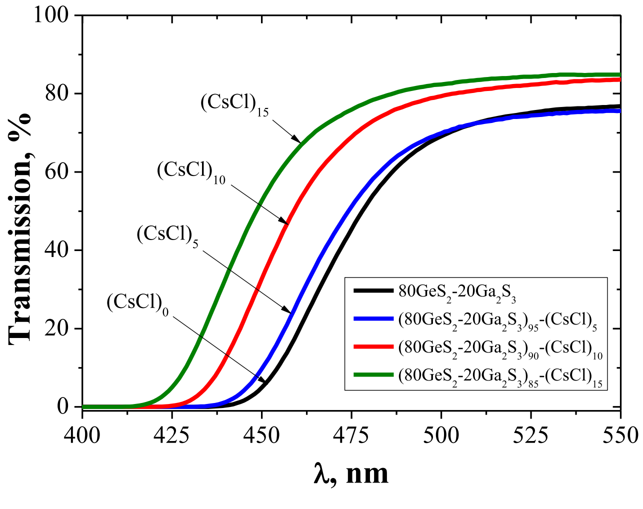

Fig. 1. Transmission spectra in the visible region of $(80GeS_2{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 15$ glasses.