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NANOSTRUCTURAL MODIFICATION OF FREE VOLUME IN CHALCOHALIDE GLASS-CERAMICS CAUSED BY CRYSTALLIZATION PROCESS

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Modification of free volume caused by crystallization process in $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ chalcohalide glass-ceramics 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 $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ glasses. Full crystallization in each of these glasses corresponds to the void constriction.

Introduction

Chalcogenide glasses with improved exploitation properties are important for novel applications [1]. Optimized inner free-volume structure of basic $GeS_2\text{-}Ga_2S_3$ glasses 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 chalcogenide glasses can be easily transformed in chalcohalide glass-ceramics transparent in IR region [2].

However, the functionality mechanism of such systems is yet unknown because their free-volume 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. 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 in materials. In this work, we are analyzing free-volume voids in initial and crystallized nanostructurally modified mixed chalcohalide $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$) compounds using PAL technique.

Experimental

The crystallization of $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ glass-ceramics was carried out at thermal annealing at (T_g + 30 °C) [2]. Transformation of free-volume defects and voids in glass-ceramics was investigated by PAL method using ORTEC spectrometer (positron source – ^{60}Co isotope) at 22 °C and relative humidity of 35 % [2,3]. Each spectrum was measured for two identical samples with a channel width of 6.15 ps and analyzed using LT 9.0 computer program. The three-component fitting procedure with lifetimes τ_1, τ_2, τ_3 and intensities I_1, I_2, I_3 was used. 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. Positron trapping parameters such as defect-free positron lifetime τ_b and positron trapping rate in defects κ_d were calculated using well-known positron-trapping model [3]. 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.

Results and Discussion

The fitting parameters and positron trapping modes for PAL spectra of initial and crystallized $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ glasses are given in Table 1. The main attention will be focused on the second defect-related component (τ_2, I_2). The lifetime τ_2 represents the size of the free-volume defects and voids in the inner structure of glasses and the intensity I_2 is proportional to the number of these defects. It is shown that for initial glass-ceramics the increase of CsCl additive in $80GeS_2\text{-}20Ga_2S_3$ matrix results in the rise of lifetime τ_2 and drop of intensity I_2. The value of positron trapping rate in defects κ_d decreases mainly due to the changes in I_2. Such changes in intrinsic defect-related structure of Ge-Ga-S glasses caused by CsCl alkali halides can be constrained by processes of atomic-deficit void agglomeration.

Table 1. PAL parameters for initial and crystallized $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ glass-ceramics

Pre-history	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.	τ_b, ns	κ_d, ns	τ_2/τ_b
$80GeS_2\text{-}20Ga_2S_3$									
initial	0.201	0.581	0.426	0.387	1.958	0.032	0.255	1.05	1.67
crystallized	0.217	0.598	0.401	0.380	1.904	0.022	0.255	0.91	1.57
$(80GeS_2\text{-}20Ga_2S_3)_{95}(CsCl)_5$									
initial	0.234	0.639	0.462	0.339	1.978	0.022	0.282	0.73	1.64
crystallized	0.221	0.699	0.424	0.287	2.026	0.014	0.257	0.63	1.65
$(80GeS_2\text{-}20Ga_2S_3)_{90}(CsCl)_{10}$									
initial	0.249	0.696	0.499	0.290	2.029	0.014	0.292	0.59	1.71
crystallized	0.232	0.695	0.446	0.292	1.948	0.013	0.270	0.61	1.65

As compared to initial and crystallized glass-ceramics for each compositions, different tendencies in transformation of PAL parameters are observed. After crystallization of $80GeS_2\text{-}20Ga_2S_3$ glass, the lifetime τ_2 shows decrease from 0.426 ns to 0.401 ns and intensity I_2 also insignificant reduces. This means that at full crystallization of base Ge-Ga-S glasses, the free-volume defects contracts and, simultaneously, their total number decrease. In other words, voids got in an unfavorable environment and the efficiency of positron trapping degrades through the exclusion or reduction (constriction) of some part of free volume. Schematic illustration of void contraction is shown in Fig. 1. In the case of $(80GeS_2\text{-}20Ga_2S_3)_{95}(CsCl)_5$ glass-ceramics the revealed changes are more evident. But in $(80GeS_2\text{-}20Ga_2S_3)_{90}(CsCl)_{10}$ samples the increasing of defect-related lifetime τ_2 is accompanied by pretty stable values of intensities I_2 in the initial and crystallized glasses (Table 1). So, the size of voids decreases but their amount is fixed. Observed transformation can be explained by void shrinking or contraction through the formation of favorable environment for transformation of voids in size without significant changes in positron trapping effectiveness. Through the comparison of defect-related parameters for crystallized $(80GeS_2\text{-}20Ga_2S_3)_{100-x}(CsCl)_x$, $0 \le x \le 10$ glass-ceramics, it is established that lifetime τ_2 rises and intensity I_2 reduces with CsCl addition. As it was in the case of initial glasses of the same compositions this confirms the agglomeration process of voids in their inner structure.

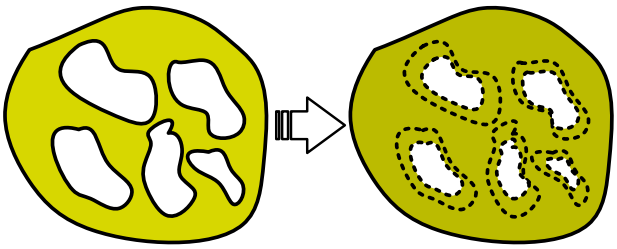

Fig.1. Schematic illustration of void constriction in Ge-Ga-S-CsCl glass-ceramics caused by their crystallization

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