Positron Annihilation Lifetime Spectroscopy in Application to Nanostructured Glasses and Ceramics

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Abstract – Modified nanostructured Ge-Ga-Se chalcogenide glasses and oxide MgO-Al₂O₃ ceramics were investigated using positron annihilation lifetime spectroscopy. It was shown that crystallization process in 80GeSe₂-20Ga₂Se₃ glasses annealed at 380•C for 25 and 50 h indicates specific free-volume transformation. It is established that water vapor modifies defects located near grain boundaries in MgO-Al₂O₃ ceramics sintered at 1300 •C, the process being accompanied by void fragmentation at water adsorption with further void agglomeration at water desorption after drying.

Keywords – ceramics, glass, positron annihilation, modification, free volume, nanovoids.

I. Introduction

Positron annihilation lifetime (PAL) spectroscopy is well-known experimental technique to study extended defects and nanovoids in solids [1]. The method is grounded on physical phenomena of positron-electron interaction in a matter. It is frequently used to identify spatial heterogeneities in crystals (dislocations, vacancies, vacancy-like clusters and agglomerates), free volume evolution in organic polymers (size and number of open-volume holes, inner pores), light metallic alloys (cracks, bubbles), zeolites, gels, etc. But this method has been rarely applied to nanostructured glasses and ceramics because of significant complications in correct interpretation of the obtained data.

The aim of this work is the investigation of inner free-volume structure in the modified Ge-Ga-Se glasses and MgO-Al₂O₃ ceramics.

II. Experimental

The PAL spectra were recorded with conventional fast-fast coincidence system (ORTEC) of 230 ps resolution (full width at half maximum FWHM of a single Gaussian, determined by ^{60}Co isotope measuring) at the temperature $T = 22$ °C and relative humidity $RH = 35$ %, provided by special climatic installation. Contribution intensity of source is 15 %. Two identical ChG samples were used to build a character sandwich arrangement needed for PAL measurements. Isotope ^{22}Na of slow activity (~50 kBq) sandwiched between two identical tested samples was used as a source of positrons [2].

A series of a few independent experiments were assembled with samples of the same thermal prehistory to exclude data scatter because of differences between actual status of samples and uncontrolled instabilities in the experimental setting of PAL spectrometer. The obtained results agreed well with each other within an experimental error-bar, being no more than ±0.005 ns in lifetimes and ±0.01 in component intensities.

The measured PAL spectra were processed with standard LT 9.0 computer program [3], the obtained curve being fitted by two components with t_1, t_2 lifetimes and I_1, I_2 intensities for glasses and four components for ceramics. Therefore, the positron trapping modes, e.g. average positron lifetimes t_{av}, positron lifetime in defect-free bulk t_b, positron trapping rate in defects k_d and fraction of trapped positrons h were calculated using a formalism of two-states trapping model [4]. For present analysis, we have developed special algorithm based on appropriate error analysis of PAL measurements geometry and background removal. In addition, the $(t_2 - t_b)$ difference was accepted as a size measure for extended free-volume defects where positrons are trapped (in terms of equivalent number of monovacancies), as well as the t_2/t_b ratio was taken in a direct correlation to the nature of these defects [2,4].

III. Results and Discussion

Typical spectrum for glasses and ceramics obtained by PAL technique is shown in Fig. 1 and Fig. 2, respectively. They are characterized by a narrow peak and region of long fluent decaying of coincidence counts in a time. The mathematical decay of such curve can be represented by a sum of decreasing exponents with different values of power-like indexes inversed to positron lifetimes [5]. According to the mathematical decomposition proposed in [5], tangent to the sites of PAL spectrum correspond to lifetimes and the area under each of these curves is proportional to the intensities.
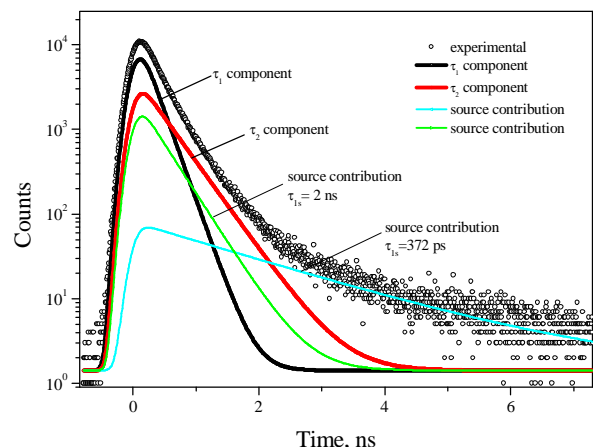

Fig. 1. Typical PAL spectrum decomposed into two components for 80GeSe₂-20Ga₂Se₃ base glass

In the case of Ge-Ga-Se glasses with extending the annealing duration to 25 h, the lifetime t_2 increases and I_2 intensity decreases due to void agglomeration. This trend reduces the positron trapping rate k_d without significant changes in $t_{av.}$ and t_b lifetimes. With further extension of

annealing duration to 50 h, the I_2 intensity increases, while lifetime t_2 decreases from 0.426 to 0.424 ns. These changes result in increased positron trapping rate k_d. The fraction of trapped positrons h decreases in the initial stage of treatment to 25 h and increases at further annealing to 50 h.

During the crystallization process at annealing for 50 h, the glass structure relaxes towards more thermodynamically favorable state. It means that free-volume nanovoids can be essentially transformed in this process. In the case of the studied ChG the fragmentation of larger free-volume entities into smaller ones occurs. Such process is accompanied by a decrease in t_2 lifetime and a corresponding increase in I_2 intensity.
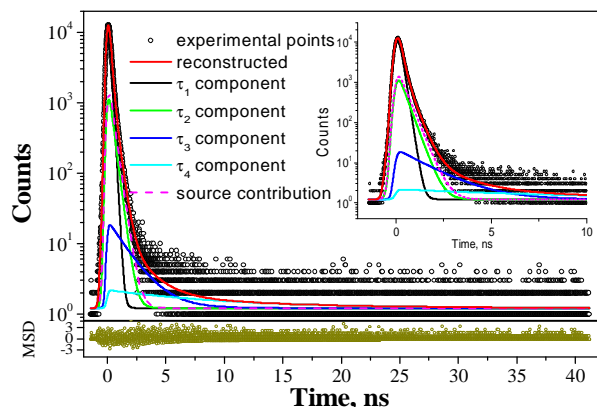

Fig. 2. PAL spectra of MgO-Al$_2$O$_3$ ceramics sintered at 1300 ^{o}C, reconstructed from four-term fitting at the general background of source contribution

Decreasing of the lifetime t_2 in water-vapored MgO-Al$_2$O$_3$ ceramics and increasing of their intensity I_2 shows intensification of positron trapping in defects near grain boundaries filled with water [2]. After drying, the intensities I_2 almost completely return to the initial values (characteristic for initially dry samples). Thus, the water-adsorption processes in MgO-Al$_2$O$_3$ ceramics are accompanied by fragmentation of positron trapping sites near grain boundaries, and respectively, the water-desorption processes are accompanied by agglomeration of free-volume voids [2].

Water-vapor sorption processes in the studied MgO-Al$_2$O$_3$ ceramics result in essential evolution of third and fourth o-Ps-related components. The intensity I_3 increases in initially dry samples after water-vapor exposure, thus confirming o-Ps annihilation in water-filled nanopores through a "bubble" mechanism (with corresponding o-Ps lifetime close to 1.8 ns). After drying, the intensities of the third and fourth components return to the initial value, confirming high efficiency of water adsorption-desorption processes. The intensity I_4 decreases in water-vapor exposed ceramics samples. After drying of the ceramic samples previously exposed to water vapor, the initial pore size tends to be restored.

Additionally, the radii R_3 and R_4 of spherical nanopores were calculated using of o-Ps-related t_3 and t_4 lifetimes in known Tao-Eldrup model [2]. The decreased t_4 value for ceramics dried after water-vapor exposure can be connected with formation of thin layers of water molecules covering the walls of pores with radii of 1.8 nm, which are not completely removed after vacuum annealing at 120 ^{o}C for 4 h.

Conclusion

Positron annihilation lifetime spectroscopy was used to investigation of free volumes in the modified nanostructured Ge-Ga-Se chalcogenide glasses and oxide MgO-Al$_2$O$_3$ ceramics. It is established that in the case of 80GeSe$_2$-20Ga$_2$Se$_3$ glasses it was shown that crystallization process during annealing at 380°C for 25 and 50 h indicates specific fragmentation of larger free-volume nanovoids into a greater number of smaller ones. In modified MgO-Al$_2$O$_3$ ceramics sintered at 1300 °C it is shown that drying of ceramics in vacuum at 120 ^{o}C previously exposed to water vapor does not restore initial pore size, confirming sensitivity of PAL method to amount of water molecules adsorbed in nanopores. The water vapor modifies defects in ceramics located near grain boundaries and this process is accompanied by void fragmentation at water adsorption with further void agglomeration at water desorption after drying. Using lifetimes of the third and fourth components of PAL spectra the radii of nanopores were calculated using Tao-Eldrup model.

Acknowledgements

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