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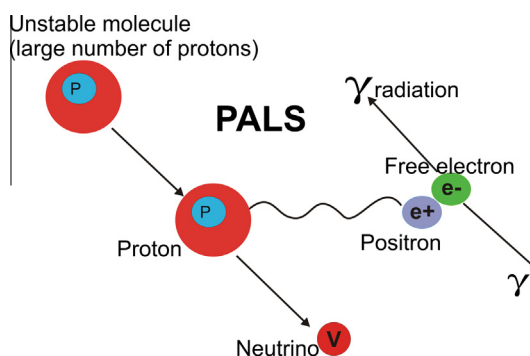
Voids in mixed-cation silicate glasses: Studies by positron annihilation lifetime and Fourier transform infrared spectroscopies [☆]

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HIGHLIGHTS

- PALS spectroscopy is sensitive for the structural changes of glass.
- The lifetime of positroniums are affected by the chemical composition of glass.
- The size of sub-nanometer-voids decreases with decreasing SiO₂ concentration.
- In the silicate glass structure there are a loosely and tightly-packed areas.
- The existence of two types of voids in silicate glass structure has been confirmed.

GRAPHICAL ABSTRACT



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ABSTRACT

PALS in comparison with FTIR studies have been applied to investigate the structure of different oxide glasses. Three components of the positron lifetime τ (τ_1 para- and τ_3 ortho-positronium and τ_2 intermediate lifetime component) and their intensities were obtained. The results of the calculation of mean values of positron lifetimes for the investigated glasses showed the existence of a long-living component on the positron annihilation lifetime spectra. From the Tao–Eldrup formula we can estimate the size of free volume. On the basis of the measurements we can conclude that the size and fraction of free volume reaches the biggest value for the fused silica glass. The degree of network polymerisation increases void size.

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Introduction

Positron annihilation is a useful technique to investigate material characteristics. In recent times PAL spectroscopy was widely used for defects characterisation of metals, polymers and topologically disordered materials without translational–orientational

symmetry such as – glasses and amorphous thin films. PALS possesses high sensitivity to the pore size in the range of 1–10 nm, moreover it is non-destructive method. The method is based on the fact that the lifetimes of a positron and its bound form, positronium (Ps), are very sensitive to the presence of defects and structural inhomogeneities in the matrix. Positrons injected into the substances, lose their energy through elastic collisions and finally annihilate with electrons through several processes. In the case of non-conductive molecular materials, in addition to the annihilation of the positron, formation an annihilation of positronium (Ps) occurs. Ps is the bound state of the positron

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and electron having an atomic radius comparable to that of the hydrogen atom. It exists in two spin states. One is called para-positronium (p-Ps) in which the positron and electron spins are anti-parallel. The other state, ortho-positronium (o-Ps), corresponds to the parallel particle spins. However, in condensed matter, the positron in o-Ps predominantly annihilates, during a collision with atoms or molecules, with an electron other than its bound partner and possesses an opposite spin. This process, called pick-off annihilation, reduces the o-Ps lifetime in glasses to a few nanoseconds. Ps cannot be formed in materials with high electron densities. The positronium formation probability and lifetime are extremely sensitive to the electron density surrounding it [1–4]. The original free volume theory for the positron annihilation in molecular substances was proposed by Brandt, Berko and Walker. The free volume was defined as the cell volume minus the excluded volume, which according to Wigner–Seitz approximations [5]. The free volume model states that Ps can only form in these free spaces of the lattice, which have the superior size to some critical values. The electron pick-off depends on the overlap of the positron component of the Ps wave function with the lattice wave function. As the size of the free volume cavity increases, the local electron density, surrounding the o-Ps, decreases. Thus the o-Ps has a slower annihilation rate and longer lifetime. Tao and Eldrup et al. derived the equation to correlate experimentally observed o-Ps life-times and free volume hole dimensions. They proposed a simple model in which the o-Ps particle resides in a spherical potential well, having an infinite potential barrier of radius R_0 . It is assumed that an electron layer forming a thickness ΔR is present within potential well of which effective radius is consequently $R = R_0 - \Delta R$ and the lifetime of the o-Ps in the electron layer is an average Ps lifetime of 0.5 ns [3,6].

Furthermore, a very successful semi-empirical equation has been established to connect the o-Ps lifetime to the size of the free volume hole in which it annihilates, thus τ_3 corresponds to a spherical space with a radius R , according to the following Eq. (1):

$$\tau_3 \text{ (ns)} = 0.5 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]^{-1} \quad (1)$$

where $\Delta R = 0.166$ nm is a fitted empirical electron layer thickness.

By fitting the above equation with the measured τ_3 values, R and free volume size V_f as:

$$V_f = \frac{4}{3} \pi R^3 \quad (2)$$

can be evaluated. The relative intensity of the longest component, I_3 is generally correlated to the density of holes, which can be considered as a kind of trapping centres for Ps. A semi-empirical relation may be used to determine the fraction of free volume (f_v) as:

$$f_v = CV_f I_3 \quad (3)$$

where V_f is the free volume calculated from τ_3 , using Eq. (1) with a spherical approximation, I_3 (%) is the intensity of long-living component and C is an empirical parameter, which can be determined by calibrating with other physical parameters [3,6].

A great number of experimental results on PAL characteristics of chalcogenide glasses (ChG), as chemical compounds from IV to V-group elements with chalcogen atoms (S, Se, Te) prepared by conventional melt-quenching method, were performed. These materials exhibited typically two positron lifetime components in the resulting PAL spectra [7,8]. In case of heavy metal fluoride glasses of varying alkali metal fluorides there is no evidence for ortho-positronium annihilation [9]. In the free volume theory, free volume in amorphous materials is assumed as the hole derived from density fluctuation of all elements. It can be considered as a constituent of the equilibrium property of the system at tempera-

tures exceeding T_g . Thus ortho-positronium formation and its lifetime were used as a tool to examine changes of local structure and free volume the temperature region approaching the glass transition. In this paper we use the o-Ps lifetime τ_3 as a sensitive parameter for variations in packing density of silicate glass with different chemical compositions. These specific kinds of structural defects can be considered as local deviations from a full saturation of covalent-like chemical bonding of a glass network, caused by destruction–polymerisation transformations or bond-switching reactions. This study is to be considered as important first step towards determining the feasibility of using PALS techniques in conjunction with FTIR spectroscopy studies.

Experimental

Bulk 66SiO₂–34Na₂O, 60SiO₂–28Na₂O–12Al₂O₃ (%mol) glasses were prepared by the conventional melt-quenching technique in an electric furnace. The batches were melted in platinum crucibles for 16–24 h at temperatures ranging from 1400 to 1550 °C. As a reference sample fused silica glass were used (Corning 7980). To remove mechanical strains developed during synthesis all samples were annealed for 1 h at their glass transition temperature. The amorphous state of prepared samples was verified by XRD measurements.

The PALS measurements were performed at room temperature using a conventional fast–fast coincidence system with an ORTEC (Fig. 1). The time resolution of the system was 270 ps (full width at half maximum). A Na²² isotope positron source of 10⁵ Bq activity was situated between two identical samples, forming a “sandwich” system.

Discriminator 5.1 line is passed to the converter start time–amplitude pulses, corresponding to the energy 1.27 MeV (signal “birth” of the positron), while the discriminator 5.2 line to stop the time–amplitude converter brings energy pulses corresponding to the 0.51 MeV (signal ‘death’ positron) and 1.27 MeV. In order to select the correct converter positron life time interval from the last dynode multiplier of one of the counters by the side line while they are fed to the converter at the input strobe pulses corresponding to the energy 0.51 MeV. Time–amplitude converter changes the interval between the pulses start (1.27 MeV) and stops (0.51 MeV) impulse voltage proportional to the time intervals. Parameters of the converter were selected in such a way that the amplitude of

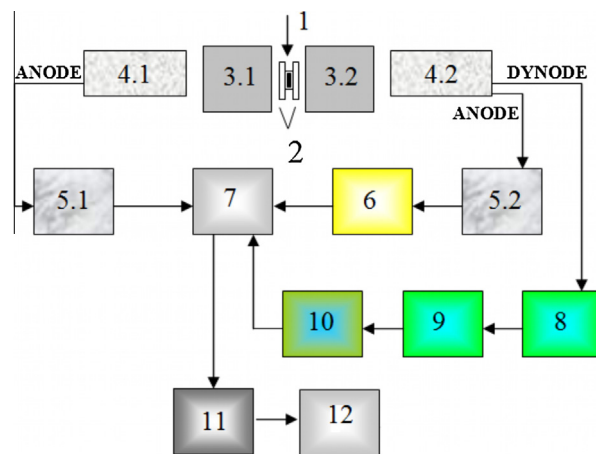


Fig. 1. Block scheme of conventional “start–stop” system of spectrometer ORTEC: 1 – Na²² source, 2 – samples, 3.1 and 3.2 – γ -scintillators, 4.1 and 4.2 – photomultipliers, 5.1 and 5.2 – constant fraction discriminators, 6 – delay line, 7 – time–pulse height converter, 8 – preamplifier, 9 – amplifier, 10 – single channel analyser, 11 – multichannel analyser, 12 – personal computer.

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