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Porous glasses as a host of luminescent materials, their applications and site selective determination

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ABSTRACT

The site selective distribution of pore sizes in pure porous glasses and glasses doped by a luminescent colorant is determined by luminescent spectroscopy, SEM, SAXS and PALS. The potential applications of the studied materials as environmental and biological sensors are outlined. We suggest how luminescent porous glasses doped by complexes of Gd can act as solid scintillators in tracing elementary particles like neutrino.

1. Introduction

Porous glasses (PG) are important in a large number of fields (neutrino detection, optics, sensors and dielectric materials). For designing these sophisticated materials properly there is a need to understand the selective distribution of sizes of the pores in doped and undoped materials. As a taste case porous vycor glasses undoped and doped by a laser dye Rot 305 are studied by steady state spectroscopy and their pore size distribution measured by PALS, SAXS and SEM. The connection between the size of the pores and the doping species is analyzed and prediction for new materials is made.

PG are an excellent medium for a large number of optically and electronically active materials and for positron signature in neutrino experiments [1]. They are prepared by chemical etching of alkali borosilicate (ABS) glasses with a two-framework structure [2,3], and are a typical example of fractal structure of dimensions between 1 and 3 [3]. They have been a subject of numerous papers dealing with fractals. The relationship between the porous space fractal dimension and the porosity of the medium has been obtained [4–6].

PG with different texture parameters (size of pores, specific surface area, and volume) can be used as membranes, adsorbents, ion-exchanger, and support materials in catalysis [7,8]. They can be used in the process of removing different impurities from gases, surface and ground water.

Impregnation of PG with different substances (metals, semiconductors, ferroelectrics, liquid crystals) gives a possibility to obtain composites with desired properties [9].

Porous silica glasses with different semiconductor, rare-earth and transition-metal impregnations are promising materials for application in optical and electronic devices as laser material, fiber lenses, solar concentrators, displays, and transparent phosphors [10–13].

Filling of PG by dye polymer gives a possibility to obtain a new class of material for laser optics.

The recent applications of PG in microelectronics, mechanical sensors, thermal insulation layers, and chemical applications are summarized by Sukas et al. [14].

Hydrophobic and highly porous materials needed for dielectrics with a reduced dielectric constant are elaborated in depts. by Baklanov group [15,16].

The numerous relaxation mechanisms processes of molecules adsorbed on porous glasses are widely studied using dielectric spectroscopy by the group by Feldman [17].

In order to design the clever materials there is a need not only to know the average size of the pores in the host materials but also the distribution of their sizes and connect them with the size of dopands and to understand their inner structure such as distribution of sizes

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of empty and filled pores. For this purpose we compare the size distribution of undoped glasses by SEM and PALS and doped glasses by PALS and luminescence spectroscopy.

The experimental procedure consists of doping the glasses, measurement by SEM, luminescent and PALS spectroscopy.

This information can be obtained either directly by SEM or extrapolate from PALS. While SEM can provide the information on the empty pores PALS can detect both empty and filled pores.

Since as mentioned before the PG can be incorporated by various optical and electronic materials it was the purpose of the present paper to compare the behavior of pure and incorporated glasses by several independent methods. The PG in this paper are incorporated by a laser dye Perylimide Red 300 the lifetimes of which was studied previously [18].

The glasses were studied by various methods: steady state absorption and fluorescence spectroscopy, scanning electron microscopy (SEM) and positron annihilation lifetime spectroscopy (PALS).

The PALS is the only method that can distinguish between the empty and filled pores. The glasses filled by a large laser dye molecules serve a model of sensors for biologically active molecules and reagents for environmental impurities.

PALS method is based on positron behavior in the medium. Positron emitted from a radioactive source (usually ^{22}Na) entering the sample can annihilate directly with one of the electrons of the medium, or it can create a bound state e^+e^- called positronium (singlet state—para-Ps, or triplet state––ortho-Ps) which locates in the regions of low electron density, called free volume.

In vacuum para-Ps decays with a mean lifetime value τ_s=0.124 ns, and ortho-Ps with τ_T=142 ns. In a solid matter the decay rates are altered by the pick-off process (e.g. annihilation of positron bound in positronium with one of the electrons of the surroundings). The pick-off process can shorten the o-Ps mean lifetime even by two orders of magnitude, depending on the free volume size.

Inside the porous silicate glasses positrons from a β^+ emitter are expected to lose most of their energies, becoming slow positrons with energies less than several electron volts in times that are small compared to their lifetimes. During the slowing down process, positrons can capture an electron from the PG within a narrow range of kinetic energies to form the atom (e^+e^-) positronium Ps. Ortho-positronium annihilate into two gamma quanta of energy 0.511 keV. Both particles disappear forming γ-rays. Using the decay it is possible to extrapolate the pore size from the model proposed by Tao [19] and Eldrup et al. [20] The model gives the possibility to determine the free volume size from the o-Ps lifetime, assuming a spherical void shape with radius R. Ps atom is trapped in the potential well whose depth is equal to Ps work function, however, for convenience of calculations it is commonly accepted to substitute that potential by infinitely deep one with radius $R_0=R+\Delta R$.

ΔR=0.17 nm is an empirically fitted parameter representing the overlap of Ps wavefunction with those of the electrons of the medium. It means that inside the void (below R value) the electron density is assumed zero, and in the layer of ΔR thickness it is constant. After these simplifications a relation between o-Ps lifetime (or decay constant) and free volume radius via pick-off process is equal [20]. A simple equation (Eq. (1)) allows obtaining the pore radii.

$$\lambda_{po}=\frac{1}{\tau_{po}}=2\left[1-\frac{R}{R_0}+\frac{1}{2\pi}\sin 2\pi\frac{R}{R_0}\right] \quad (1)$$

Eq. (1) is commonly used, e.g. for determination of the free volume expansion in polymers. It can be also useful in investigations of any kind of PG.

The exotic use of PG doped by complexes of Gd can be considered for detectors for elementary particles like neutrino. This is based on the following reasons. In inverse β-decay used in the experiments neutrinos are created due to the reaction

$$\bar{\nu}_e + p \rightarrow e^+ + n \quad (2)$$

which follows by γ-radiation due to neutron–proton coincidence

$$n + p \rightarrow d + \gamma \quad (3)$$

The reason for addition of Gd is following. Neutrino has a very low cross section $\sigma \sim 10^{-42}$ cm^2 (M. Vagins). Therefore adding Gd as a complex to the PG could increase the sensitivity of the detection of the reaction. Loading gadolinium to the material causes enhancement of the neutron detection as Gd has a high neutron capture cross-section.

$$\begin{array}{l} \bar{\nu}_e + p \rightarrow e^+ + n \\ \qquad\qquad\qquad\quad \downarrow \\ n + {}^{A}Gd \rightarrow {}^{A+1}Gd + \gamma's \end{array} \quad (4)$$

which means that the γ-rays emitted from PG due to reactions (3) and (4) can form a valuable source of fluorescent excitation in solid detectors.

So far in a number of experiments concerning electron antineutrinos detection liquid scintillators are applied. In the liquid scintillators used in inverse β-decay both neutron and positron are detected in coincidence (neutron is captured on protons and positrons annihilate with electrons). As it was explained in detail in the paper by Franco et al. [1] solid detectors can be most effective in such experiments. PG doped by Gd are a promising material to such an application. In porous materials positron can create positronium which is trapped in the pores. This gives the possibility to detect annihilation of positronium (mainly orthopositronium) what leads to lengthening the positron lifetime value to a few or even tens of nanosecond.

2. Experimental

For our experiments two types of PG samples were used: undoped and doped by laser dye Rot 305.

The dimensions of the samples were $10\times10\times(0.5–1.0)$ mm^3. The glasses were obtained previously by leaching out alkali borosilicate glass [3] with a solution 3 M HCl+0.5 M KOH.

An identical sample of PG was doped by a laser dye Rot 305 by dipping the glass in a solution of Rot 305 for 2 h, draying by 80 °C for 1 h. The concentration of the starting dye solution of Rot 305 in chloroform was 2.79×10^{-6} M. The structural formula of laser dye Rot 305 is shown in Fig. 1 and its calculated area is around 1 nm^2 [21].

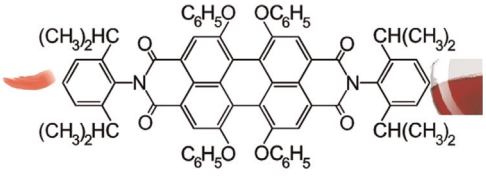

Fig. 1. The structural formula of Rot 305 (Lumogen F Red 305) (perylene-1,8,7,12-tetraphenoxy-3,4,9,10-tetracarboxylic acid bis-(2′,6′-diisopropylanilide)).