NUKLEONIKA 2013;58(1):241–244

ORIGINAL PAPER

Porosity structure in photon active glasses

Bożena Jasińska,
Monika Śniegocka,
Renata Reisfeld,
Elena Zigansky

Abstract. Two kinds of photon active glasses were investigated using positron annihilation lifetime spectroscopy (PALS). Both kinds of glasses were prepared using a sol-gel technique, doped by complex of ruthenium tris bipyridyl chloride. Glasses differed from the initial matrix: the first one was prepared using silicon oxide while the second one – zircon oxide. The *ortho*-positronium (*o*-Ps) lifetime and intensities were determined from lifetime spectra. Different porosity structure concluded from PALS measurements was found in both cases. In the silica based glasses small free volumes (angstrom size) and pores (from 1 to 10 nm) existed in the material. On the contrary, in zirconia based glasses small intermolecular voids were produced in the structure only, independently of the way of material preparation.

Key words: glass • *ortho*-positronium (*o*-Ps) • porosity • positron annihilation lifetime spectroscopy (PALS) • sol-gel technique

B. Jasińska✉, M. Śniegocka
Institute of Physics,
Maria Curie-Skłodowska University,
1 M. Curie-Skłodowskiej Sq., 20-031 Lublin, Poland,
Tel.: +48 81 537 6288, Fax: +48 81 537 6191,
E-mail: bozena.jasinska@poczta.umcs.lublin.pl

R. Reisfeld, E. Zigansky
The Hebrew University of Jerusalem,
91904 Jerusalem, Israel

Received: 31 July 2012
Accepted: 16 October 2012

Introduction

Positron annihilation lifetime spectroscopy (PALS) is a technique based on positron behaviour in the medium. Since a simple relation between *ortho*-positronium (*o*-Ps) lifetime and void radius was proposed by Tao [9] and Eldrup *et al.* [3], it has become a popular tool in investigations of free volumes in solids. In polymers for example, it is applied to observe free volume distribution and phase transition [2]. The model mentioned above gives the possibility to determine the free volume size from the *o*-Ps lifetime value, assuming a spherical void shape with radius *R*. Ps atom is trapped in the potential well whose depth is equal to Ps work function. In the last 10 years PALS began to be applied to porous materials. Such a possibility was opened by the so-called extended Tao-Eldrup model (ETE) [1, 4]. It assumes cylindrical or spherical pore shapes and, in the case of larger size (over 1 nm) takes into account the possibility of population of the excited states in the potential well. If thermal equilibrium is achieved, one should observe a single decay rate averaged over all populated states. It is worth mentioning that because population of the excited level is temperature dependent, the model explains lowering of *o*-Ps lifetimes with increasing temperature, as observed in porous media. The possibility of applying various shapes of the pores in ETE model as well as in the porosimetric techniques allows for using both methods to investigate porous materials.

All kinds of porous media are intensively investigated as they are widely used in industrial and technical applications. The subject of this paper was to compare the porosity structure in photon active glasses prepared using two various initial material: silicon oxide or silicon-zircon oxide. Our glasses exhibit absorption and emittion of spectra for photonic materials.

Experimental

Samples of porous glass produced using a sol-gel technique were investigated using the PALS technique. Two initial matrices were used to produce the porous glass: silicon or complex silicon and zircon oxides. The initial material was doped by ruthenium tris bipyridyl chloride. Depending on a catalyst (HCl, HF or HNO_3), a temperature of treatment, and conditions of hydrolysis, one obtains various porosity and pores distribution in the created material [7, 10]. A comparison of the room temperature results by PALS with those by the liquid nitrogen adsorption method in silica based glass were presented elsewhere [8].

Samples were measured using PALS in the temperature range from 100 to 500 K. The samples of glass were placed in a vacuum chamber, under a pressure of ~0.5 Pa. Lifetime spectra were collected by using a fast-slow spectrometer with BaF_2 scintillators. The spectra were recorded in the range of 1 μs the channel definition was 117 ps (or in the range of 100 ns, the channel definition was 11 ps). The data were processed by the LT program [6].

The spectra were decomposed into 3 or 4 components depending on the recorded range (the measured lifetimes value). In a three component fit, the first component comes from *para*-positronium (*p*-Ps) decay, the second one from free annihilation and the longest lived one comes from *o*-Ps decay. In a four-component fit the two longest lived are related to *o*-Ps decay: the shorter one of these two, with a lifetime from 1.5 to 5 ns is related to *o*-Ps annihilation in small intermolecular voids and the longest lived one – to the annihilation in the pores.

In this paper the *o*-Ps components are discussed only.

Results and discussion

Two series of glass samples prepared using as an initial matrix different oxides show different porosity structure seen by positron annihilation lifetime spectroscopy. In both kinds of glasses positronium is formed in the whole range of temperatures, but its lifetime value is dramatically different. In silica-zirconia matrix one *o*-Ps component exists in the spectrum, its lifetime value does not exceed a few nanoseconds. In glass produced on silica matrix two *o*-Ps components can be found and *o*-Ps lifetime values reached 100 ns.

The *o*-Ps lifetime and intensity values in the temperature range from about 100 to 500 K in one chosen glass sample produced with complex matrix are shown in Fig. 1. Both parameters rise in the whole range of temperatures, but the tendency is not monotonous. The biggest change of the *o*-Ps lifetime value is seen between

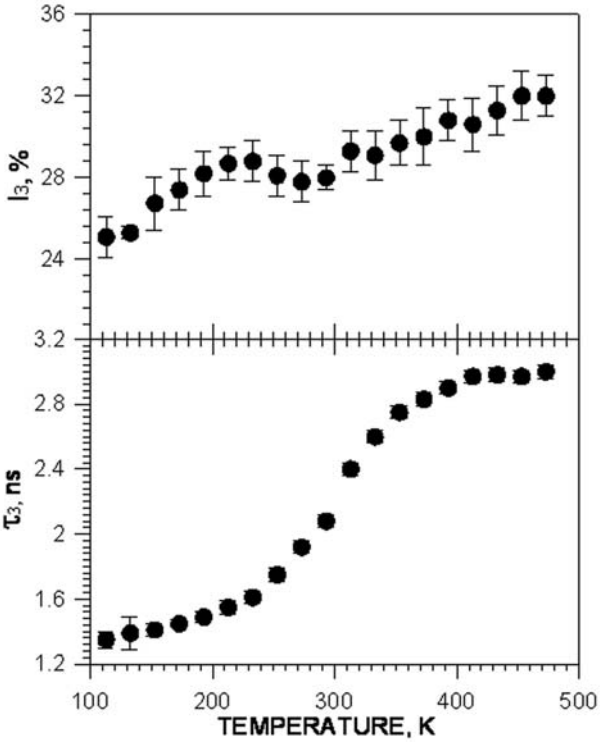

Fig. 1. The *o*-Ps lifetime and intensity in the glass sample prepared with a matrix of silicon-zircon oxides.

200 and 300 K, while intensity value in this range almost does not change. This may mean that the total volume accessible for positronium trapping is much wider at higher temperatures. From the lifetime value equaling to 2.1 ns at room temperature, using Tao-Eldrup model [3, 9] one can determine a void radius of about 0.3 nm. It is the typical volume size found in amorphous materials. In other glasses produced from the same matrix similar temperature dependencies of *o*-Ps lifetime and intensity were found.

Three samples containing the pores of different radii were chosen to present experimental dependencies of *o*-Ps lifetime and intensity on temperature in glasses prepared on silica matrix. In Figs. 2 and 3 both *o*-Ps components of the selected glass samples are presented. The first *o*-Ps component (Fig. 2) can be ascribed to *o*-Ps decay in small intermolecular voids, always present in an amorphous material. The lifetime values reached 5 ns at the highest temperatures in one of the glasses. Temperature dependencies of *o*-Ps lifetime are linear, lines in the figure are fitted to experimental points. In polymer investigations such a dependence is usually treated as related to thermal expansion of the material. Using the Tao-Eldrup formula, from the range of changes of *o*-Ps lifetime one can determine respective changes of void radii. In the case of glass No. 1 lifetime, value increases from 1.6 to 2.6 ns, it means that the void radius rise from 0.25 to 0.34 nm. For glass No. 2, changes of lifetime from 2.0 to 2.85 ns correspond to the rise of radius from 0.29 to 0.36 nm. And for glass No. 3, increase of lifetime from 3.3 to 4.3 ns corresponds to a radius value increase from 0.39 to 0.45 nm. Increase of lifetime value coming from thermal expansion of the material would mean 20–30% increase of void radius.

The next component is related to *o*-Ps decay in the pores. At room temperature measurements, the *o*-Ps

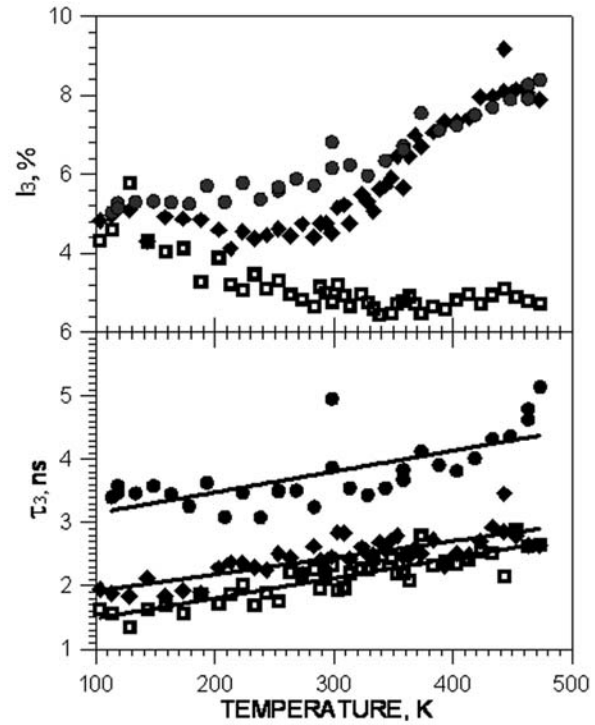

Fig. 2. The *o*-Ps lifetime and intensity in the small intermolecular voids for the glass samples prepared with a silica matrix. Symbols denote: full dots – the glass sample No. 1, open squares – the glass sample No. 2, diamonds – the glass sample No. 3.

lifetime in the pores, τ_4, was found to be 18.8 ns in the first glass, 42.3 ns in the second one and 63.2 ns in the third glass. The pore radii deduced from the ETE model, assuming cylindrical shape of voids for such lifetimes are equal to 0.79, 1.20 and 1.78 nm, respectively, while for spherical shape the radii should be 0.99, 1.55 and 2.38 nm. The determination of the shape of the pores in the glass produced by the sol-gel technique is not a simple problem. From our previous paper [8], where we compare results of PALS and liquid nitrogen adsorption/desorption, it comes that the shape of the pores is very complicated and both techniques give a different size, for example in the case of the bottle-shape pores. In some glass samples closed pores exist which are seen only by PALS. In the other paper [5] we tried to discuss such problems from temperature dependencies of *o*-Ps lifetimes in the pores using the ETE model, but results are also unequivocal. From Fig. 3, one can see that *o*-Ps lifetime value in all glasses decrease. This is an effect of temperature dependence of population of the excited states in the potential well. The intensity values in all glasses increase with temperature, in one case reaches almost 30%. In means that in the investigated material a great amount of the pores exists in which positronium can be trapped.

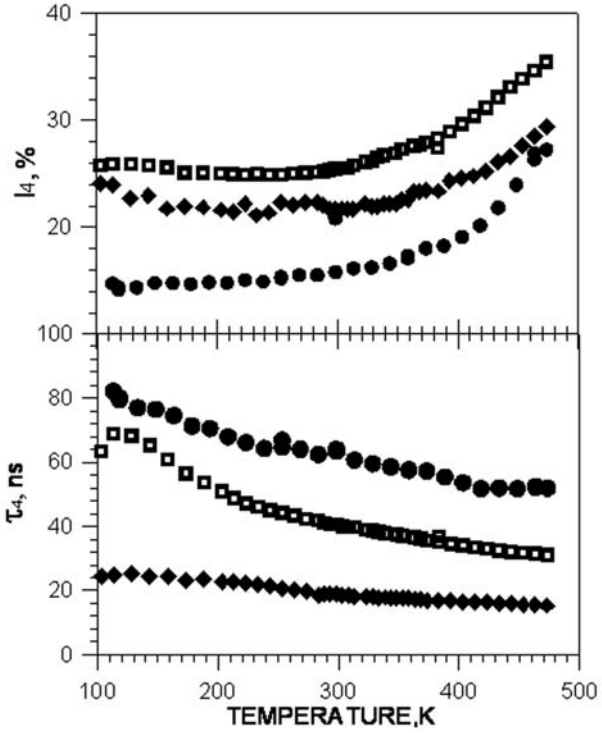

Fig. 3. The *o*-Ps lifetime and intensity in the pores for the glass samples prepared on a silica matrix. Symbols denote: full dots – the glass sample No. 1, open squares – the glass sample No. 2, diamonds – the glass sample No. 3.

Conclusions

Positron and its bound state positronium can be successfully used in investigations of materials with complicated porosity structure. Each kind of voids/pores results in the addition of a new component in positron lifetime spectrum. From lifetime value, one can determine free volume size. ETE model extends such a possibility to the class of porous media. From the intensity value, one can determine the amount or sometimes the number of the voids.

From our investigation, it comes that one of the main parameters influencing porosity structure of the glass produced using the sol-gel technique seems to be the matrix used for material preparation.

Acknowledgment. This paper was supported by a grant No. N N204 131137.

References

1. Ciesielski K, Dawidowicz AL, Goworek T, Jasińska B, Wawryszczuk J (1998) Positronium lifetimes in porous Vycor glass. Chem Phys Lett 289:41–45
2. Consolati G (2001) An experimental investigation of the occupied volume in polymers. Mater Sci Forum 363/365:244–247
3. Eldrup M, Lightbody D, Sherwood JN (1981) The temperature dependence of positron lifetimes in solid pivalic acid. J Chem Phys 63:51–58
4. Goworek T, Ciesielski K, Jasińska B, Wawryszczuk J (1997) Positronium in large voids. Silica gel. Chem Phys Lett 272:91–95
5. Jasińska B, Zaleski R, Śniegocka M, Reisfeld R, Zigansky E (2007) Testing ETE model, temperature dependences of PALS data. Phys Status Solidi C 4;10:3985–3988
6. Kansy J (1996) Microcomputer program for analysis of positron lifetime spectra. Nucl Instrum Methods A 374:235–244
7. Reisfeld R (2001) Prospects of sol-gel technology towards luminescent materials. Opt Mater 16;1/2:1–7

8. Reisfeld R, Zigansky E, Jasinska B, Wodnicka K (2005) Porosity of sol-gel silica glasses doped by ruthenium bipyridyl as measured by positron annihilation lifetime spectroscopy and nitrogen adsorption. Opt Appl 35;4:677–689
9. Tao SJ (1972) Positronium annihilation in molecular substances. J Chem Phys 56:5499–5501
10. Yariv E, Reisfeld R, Saraidarov Ts, Axelrod E, Rysiakiewicz-Pasek E, Wodnicka K (2002) Optimization of tunable laser glasses with the aid of dielectric relaxation and adsorption measurements. J Non-Cryst Solids 305:354–361