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Investigation of the structure of gallium oxide glasses by means of positron lifetime measurements

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Positron lifetime spectroscopy PALS has been applied to the investigation of the structure of gallium oxide glasses. Three components of the positron lifetime τ (τ_1 *para-* and τ_3 *ortho-positronium* and τ_2 *average living component)* and its intensities *I* were obtained. The analysis shows that the obtained lifetime components correspond to the occurrence of free volume holes (τ_1 and τ_3) and positron trapping in vacancy-type defects (τ_2). From the Tao-Eldrup formula we can estimate the size of the free volume. The percentage of intensities of the individual components of the positron lifetime shows that it is strongly dominated by vacancy-type defects.

Gallium oxide glasses / Positron annihilation / Positronium / Structure of glasses

Introduction

One of the most active fields in solid state research in recent years is the study of amorphous materials. The aim of this paper is to understand the changes induced by Pb and Bi in heavy metal oxide (HMO) glasses, using positron annihilation lifetime spectroscopy (PALS). Positron annihilation is a useful technique to investigate material characteristics. Positrons injected in substances lose their energy through elastic collisions and finally annihilate with electrons through several processes. In the case of non-conductive molecular materials, formation and annihilation of positronium (Ps) take place in addition to the annihilation of the positron. Ps is the bound state of the positron 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 parallel particle spins. The process, called pick-off annihilation, reduces the o-Ps lifetime in polymers to a few nanoseconds. Ps cannot form in materials with high electron densities. The positronium formation probability and lifetime are extremely sensitive to the electron density surrounding Ps. The o-Ps localises in the space between and along polymer chains and at chain ends (free volume holes), and the lifetime gives an indication on the mean radii of these holes [1-4]. The original free volume theory for the positron annihilation in molecular substances was proposed by Brandt, Berko and Walker [5]. Thus the o-Ps has a slower annihilation rate and longer lifetime. Tao and Eldrup *et al.* [6,7] derived an equation to correlate experimentally observed o-Ps lifetimes and the dimensions of free volume holes, mainly in polymers.

Glasses based on oxides of germanium, gallium, tellurium and antimony are often referred to as heavy metal oxide (HMO) glasses. They are promising materials for photonics and optoelectronics, as passive and optical fibres, and for optical switching, due to their smaller phonon energy and larger refraction indices than silicate glasses [8,9]. Gallium bismuthate glasses appear to be promising host materials for waveguide devices in microwaves telecommunication windows, broad band amplifier and high power laser applications [2]. They offer better chemical stability than fluoride glasses. Glasses including gallium systems are characterized by high optical nonlinearity, high magneto-optic effect and extended IR transparency. Ga_2O_3 is a heavy metal oxide, and when it is introduced in the glass matrix, it may influence the physical properties. Many recent investigations on the role of Ga_2O_3 in various glass matrixes are available in the literature [8-11]. Lead and bismuth cations have the greatest mass and the smallest field strength among the non-radioactive cations, but their oxides themselves do not form glasses under normal cooling conditions. It is necessary to add a stabilizer, whose role in the investigated glasses meet gallium oxide [12]. The structure of heavy metal oxide glasses

is interesting because such information helps better understanding glass processing [8].

Experimental

Two PbO–Bi_2O_3–Ga_2O_3 glass systems were prepared by using reagent grade chemicals Bi_2O_3, Ga_2O_3 and PbO as starting materials (Table 1). The homogenised mixtures were melted at 1100°C in covered platinum crucibles in an electric furnace and then the melts were quickly undercooled at room temperature by pouring onto stainless-steel plates. The melting time was 30 min. The glass transition temperatures (T_g) and crystallization temperatures (T_{cr}) of the samples were determined in the temperature range 20-1000ºC using a Perkin Elmer DTA 7 device. Differential thermal analysis (DTA) traces were recorded at the heating rate 10°C/min (Fig. 1). The amorphous state was confirmed by X-ray diffraction using a DRON-1.5 diffractometer (Fig. 2).

The PALS measurements were performed at room temperature using a conventional fast–fast coincidence system with an ORTEC spectrometer. The time resolution of the system was 0.270 ps (full width at half maximum). Each specimen consisted of a system of circular layers, of total size 10 mm diameter and 1.2 mm thickness. A ^{22}Na isotope positron source of 7.4×10^5 Bq activity was situated between two samples, forming a "sandwich" system. In general, each PALS spectrum, recorded with a total number of

Table 1 Chemical composition of the investigated PbO–Bi_2O_3–Ga_2O_3 glasses.

Glass No.	Glass composition [mol.%]		
	PbO	Bi_2O_3	Ga_2O_3
1	60	10	30
2	20	50	30

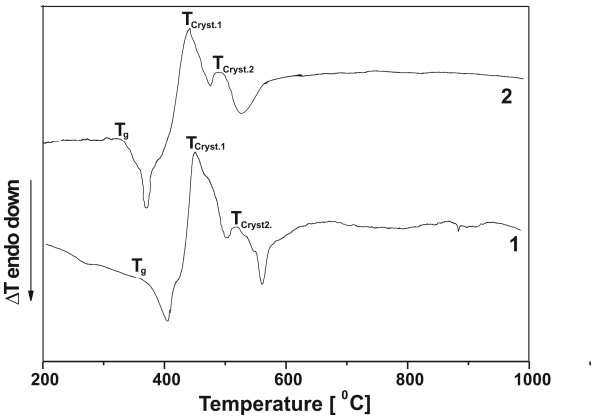

Fig. 1 DTA curves of PbO–Bi_2O_3–Ga_2O_3 glasses.

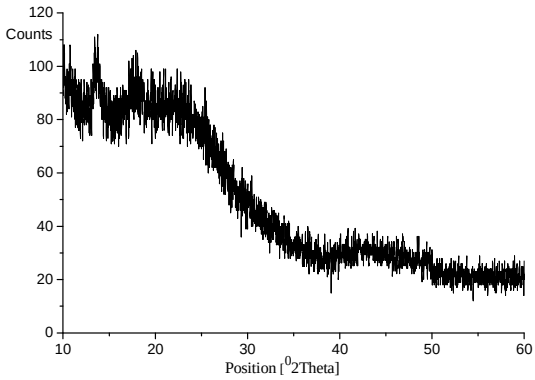

Fig. 2 XRD pattern of the green glass 1.

2×10^6 counts, which is high enough to obtain a good analysis, was measured five times to check its reproducibility. The lifetime spectra were analysed by the common "Microcomputer program LT" designed by Kansy [13].

Results and discussion

Analysis of the DTA curves of glasses 1 and 2 indicates, besides the thermal effects characteristic (Table 2) of phase transitions occurring in glassy materials, very strong exothermic peaks near 468 and 509ºC (Fig. 1). The thermal stability parameter ΔT was calculated for both glasses. The value of ΔT is higher for glass 2, which indicates that glass 2 is characterized by higher thermal stability.

The positron lifetime spectra were analyzed using the LT computing program with a three-component model (Fig. 3 shows a typical lifetime spectrum). Therefore, only three-component results are presented here. In glass materials, the short-lived component is usually attributed to p-Ps annihilation. Therefore, the shortest lifetime τ_1 was fixed at 125 ps (the p-Ps lifetime) during the fitting. The intermediate lifetime ($\tau_2 \sim 0.3$ ns) is due to the annihilation of free positrons with electrons in the bulk material and positron trapping modes [4,14-16]. The results of the calculation of the mean values of the positron lifetimes for the investigated samples showed the existence of a long-lived component in the positron annihilation lifetime spectra.

According to the common interpretation we attribute the longest component τ_3 to the pick-off annihilation of o-Ps trapped by free volumes. In any given sample, all the free volume holes are not of the same size. The LT results are the averaged values, but the real long-lived annihilation events have some time-distribution around the averaged value. So, the concept of the average free volume size is used in practice. The variations of the intermediate lifetime τ_2

Table 2 Thermal characteristics of $PbO–Bi_2O_3–Ga_2O_3$ glasses.

Glass No.	T_g [°C]	$T_{max\ cr1}$ [°C]	$T_{max\ cr2}$ [°C]	$\Delta T_1 = T_{max\ cr} - T_g$ [°C]	$\Delta T_1 = T_{max\ cr} - T_g$ [°C]
1	390	468	509	78	119
2	345	467	490	122	145

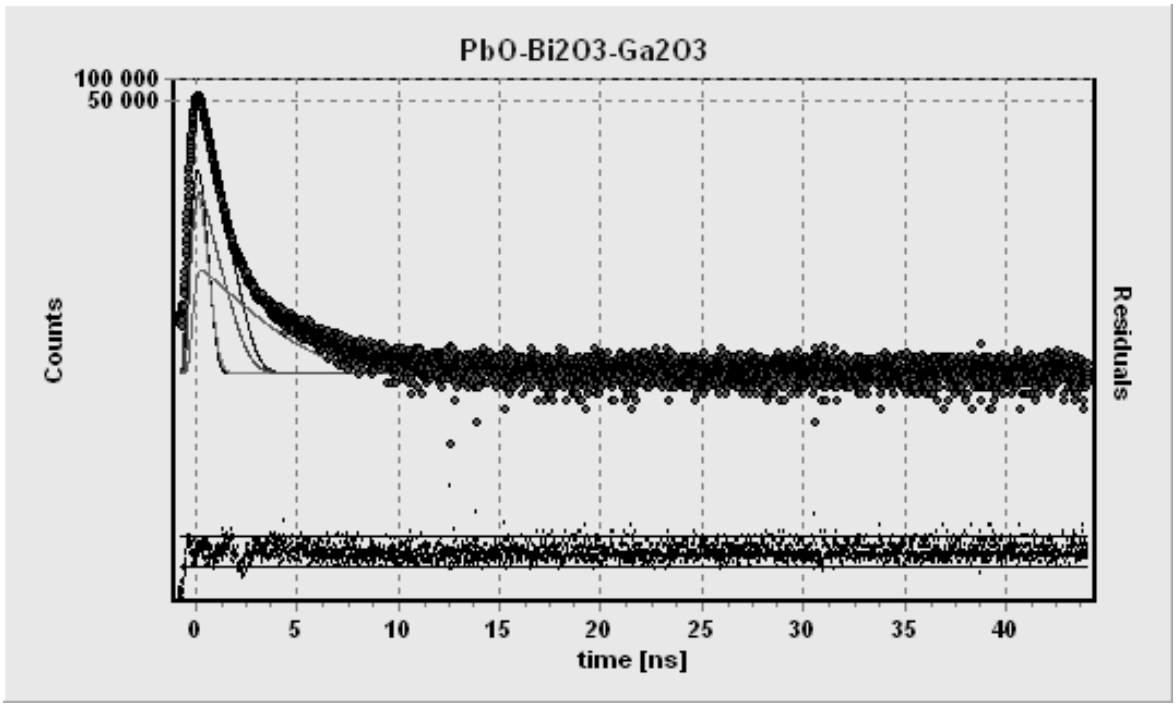

Fig. 3 Typical lifetime spectrum for the investigated $PbO–Bi_2O_3–Ga_2O_3$ samples.

Table 3 Mean values of the lifetimes τ_2, τ_3 and relative intensities I_2, I_3 for $PbO–Bi_2O_3–Ga_2O_3$ glasses.

Glass No.	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]
1	0.324 ± 0.0064	92.180 ± 0.042	2.321 ± 0.014	2.216 ± 0.019
2	0.318 ± 0.0065	93.789 ± 0.044	2.003 ± 0.012	1.307 ± 0.018

and o-Ps pick-off lifetime τ_3 and theirs intensities for the investigated samples are presented in Table 3.

The studies show that in samples 1 and 2 the component τ_2 does not change beyond the limits of the experimental errors. The value of the longest component τ_3 and its intensity I_3 are much higher in the case of glass 1. This can be explained by the arrangement of PbO in the glass structure. PbO plays the role of glass former and makes the structure looser. In the case of glass 2 PbO acts as a glass former and modifier that thickens the structure. Further investigations of gallium oxide glasses using PALS techniques will include glasses with other percentages of PbO and Bi_2O_3. Structure investigations will allow improving the production of glasses for technological applications including gallium systems characterized by high optical nonlinearity and high magneto-optic effect.

References

[1] Y.C. Jean, *NATO Advanced Research Workshop, Advances with Positron Spectroscopy of Solids and Surfaces*, Varenna, Italy, July 16-17, 1993.
[2] R.A. Pethrick, *Prog. Polym. Sci*. 22 (1997) 1.
[3] M. Hyla, J. Filipecki, Z. Mandecki, R.I. Mervinskii, *J. Non-Cryst. Solids* 232-234 (1998) 446-449.
[4] M. Hyla, J. Filipecki, J. Swiatek, *J. Non-Cryst. Solids* 352 (2006) 2726-2230.
[5] W. Brandt, S. Berko, W.W. Walker, *Phys. Rev.* 120 (1960) 1289-1299.
[6] S.J. Tao. *J. Chem. Phys*. 6 (1972) 5499-5506.
[7] M. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys*. 63 (1981) 51-58.
[8] D. Dorosz, *Mol. Quant. Acoust.* 25 (2004) 79-87.

[9] D. Lezal, J. Pedlikova, P. Kostka, J. Bladuska, M. Poulain, J. Zavadil, *J. Non-Cryst. Solids* 284 (2001) 288-295.
[10] C.T. Tan, T.N. Ooi, S.K. Lahiri, *J. Mater. Sci. Lett.* 14 (1995) 405-407.
[11] M. Janewicz, K. Kopczyński, Z. Mierczyk, *Proc. SPIE* 1793 (1992) 158.
[12] S. Simon, V. Simon, *Mater. Lett.* 58 (2004) 3778-3781.
[13] J. Kansy, *Nucl. Instr. Meth. Phys. Res. A* 374 (1996) 235-244.
[14] R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors*, Springer, Berlin, 1999.
[15] B. Bergersen, M.J. Stott, *Solid State Commun*. 7, (1969) 1203-1208.
[16] R. Krause-Rehberg, H.S. Leipner, *Appl. Phys. A* 64 (1997) 457-462.

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