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EPR study of gamma irradiated yttrium bioactive glasses and yttrium silica sol-gel microspheres

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Silica bioactive glasses and sol-gel silica microspheres containing neutron activable yttrium were investigated as a potential material for internal radiotherapy of cancer. Yttrium bioactive glasses were obtained by melts annealing method while yttrium silica microspheres by sol-gel and spray-drying techniques. Information about the local structure of the samples was obtained by EPR investigation of the gamma radiation-induced paramagnetic defects in the structure of the samples. The EPR spectra of gamma irradiated the melted yttrium bioactive glasses indicate the presence of HC_1 and HC_2 non-bridging oxygen hole centres in their structure. These defect centres are related to the presence of Q^1 and Q^2 units in the structure of the glasses. The presence of small amount of boron oxide, in some of the glasses induced the formation of boron oxygen hole centres (BOHC) and boron electron centres (E'). In the structure of sol-gel yttrium silica microspheres thermally treated at 700 ^oC, two paramagnetic defect centres, non-bridging oxygen hole (NBOHC) and O_2^- centres, were evidenced after gamma irradiation.The presence of the EPR evidenced defects have to be taken into account as possible centres for glass dissolution in human body during the radiotherapy procedure.

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1. Introduction

Physical properties of the glasses can change when they are subjected to ionizing radiation. The kind and the extend of the properties variations depend on the kind of radiation and also on the composition of the glasses [1]. The result of exposure to ionizing radiations such as neutrons, protons, energetic electrons, γ-rays, X-rays, or sometimes even UV-light is the generation of paramagnetic defect centres. These defect centres may comprise, for example vacancies and interstitials in an otherwise perfect random network. Such displaced atomic species may be created by the radiation or they may be pre-existing in the glass. In both cases they are rendered paramagnetic by the trapping of radiation-generated electrons or holes [2].

Defect centres in glasses can be E'centres, peroxy radicals and non-bridging oxygen hole centres (NBOHC). The E' centre can be described by an electron trapped by a silicon atom facing an oxygen vacancy. The peroxy radical can be the anti-defect of the E' centre. Hydroxyl ions could be also the precursors of the peroxy radical centres. The non-bridging oxygen centre (NBOHC) can be generated via strained oxygen bridges [2,3].

The structure of the radiation-induced paramagnetic defect centres are themselves strongly related to the structure of the unirradiated glass [2]. Detection and characterization of these paramagnetic centres delivers valuable information about the structure of glasses synthesized by either melting or sol-gel techniques [4].

In the EPR spectra of alkali silicate glasses, two types of defect centres, HC_1 and HC_2, have been distinguished and assigned to holes trapped on non-bridging oxygen (NBO) atoms [5-8]. It is well known that the structure of amorphous silica consists of SiO_4 units in which a silicon atom is in a tetrahedral configuration with four bridging oxygen atoms. The addition of even small amounts of alkali oxides causes the start of the destruction of the polymerized silica network because of breaking of Si-O-Si bonds throughout the structure. Thus SiO_4 tetrahedral units are created with one, two or more non-bridging oxygen atoms resulting from the presence of the continuous increasing amount of network modifying cations. For the first defect centre HC_1, most of the proposed models supported the fact that it is a hole trapped on a silicon-oxygen network tetrahedron which has three bridging atoms and one NBO and with one network modifier cation nearby. On the contrary, for the second defect centre HC_2 the models assume that the hole is trapped on two NBO atoms bonded to the same silicon of a SiO_4 unit. Due to the fact that the existence of two defect centres is related to the formation of tetrahedral units with one or two NBO atoms, the change in the glass network and the effect of thermal history has on it could be observed through the EPR spectroscopy [6,7].

The structure of defects in sol-gel-derived glasses might be unlike from that of molten glasses in which the melt structure and thermal history play important roles in influencing the nature and concentration of defect centres. However, the defect centres in glasses prepared by sol-gel can be also E' centres, peroxy radicals and non-bridging oxygen hole centres (NBOHC) as for the glasses prepared by melting technique [4,9-11].

The precursors for the peroxy radical and NBOHC are believed to be an oxygen surplus site (O_3Si-O-O-SiO_3) and a hydroxyl site (O_3SiO-H) respectively. Brinker et al. suggested that strained cyclic trisiloxanes (three-membered rings) are also precursor structures to E' centres and oxygen hole centres [12,13].

The present study proposes the investigation of the local structure of the several melt-derived yttrium bioactive glasses and sol-gel non-crystalline microspheres by EPR spectroscopy. The paramagnetic defect centres were induced by exposure of the samples to gamma radiation.

2. Experimental

The yttrium bioactive glasses were obtained by adding different amount of yttrium oxide to several bioactive glass compositions. The glass samples were prepared by mixing the analytical grade Na_2CO_3, K_2CO_3, MgO, $CaCO_3$, $CaHPO_4(2H_2O)$, Y_2O_3 and commercial Belgian quartz sand and melting the batches in a Pt- crucible at 1360°C for 3 hours. For the glass with high yttrium oxide content (LYS) the melting temperature was 1450 °C. The glasses were cast, annealed, crushed and remelted to improve their homogeneity. The composition of the yttrium-containing bioactive glasses is given in Table 1.

Table 1. The composition of yttrium bioactive glasses (wt%).

Glass	HY1.1	HY2	HY3	HY4	LY3	LYS
SiO_2	46.09	43.91	43.91	44.35	51.74	53
Na_2O	5.22	13.04	17.39	21.74	4.35	6
P_2O_5	3.48	0.87	0	0	0	2
CaO	17.39	15.22	15.22	13.04	21.74	10
B_2O_3	0	0.87	0	2.61	0	0
K_2O	10.43	13.04	6.52	0	6.52	12
MgO	4.35	0	3.91	5.22	2.61	2
Y_2O_3	13.04	13.04	13.04	13.04	13.04	15

Silica microspheres of less than 50 μm of diameter incorporating yttrium were prepared by sol-gel and spray-drying methods. The investigated samples contain 16.6 wt % yttrium oxide. The sols were obtained by the hydrolysis and polycondensation of tetraethoxysilane (TEOS 98 %, Aldrich) and yttrium (III) nitrate hexahydrate 99,9 % ($Y(NO_3)_3 \cdot 6\ H_2O$) used as precursors. The nitrate was dissolved in a water or water/ethanol mixture (molar ratio 1:7) and hydrochloric acid (0.002M) was used as a catalyst. Microspheres were obtained by spraying yttrium silica sols with a Buchi-191 mini spray-dryer. The sol-gel and spray-drying parameters are given in Table 2. The as-prepared microspheres were thermally treated at 700 °C for 3 hours.

Table 2. The sol-gel and spray-drying parameters.

Sample	Sol-gel parameters				Spraying parameters			
	R_1	R_2	pH_f	r	P (%)	A (%)	F (l/h)	T_i (°C)
SiY05	22	30	1.7	0	16	95	400	150
SiY06	30	38	2.0	0	16	95	400	150
SiY09	61	91	3.3	0	16	95	400	170
SiY12	61	91	3.6	1:7	16	95	400	170

R_1-initial H_2O/TEOS ratio, R_2-final H_2O/TEOS ratio, r-TEOS/EtOH ratio, P-pump, F-flow, A-aspirator, T_i-inlet temperature.

The investigated glass samples were exposed to ^{60}Co γ-ray irradiation, at room temperature to generate paramagnetic centres. The melt-derived glass samples were given doses up to 1.7 kGy and the sol-gel samples doses up to 1.3 kGy. The EPR measurements were carried out on a Portable Adani PS800 spectrometer operating in X band (υ = 9.37 GHz).

3. Results and discussion

3.1. EPR study of yttrium bioactive glasses

Figs. 1 and 2 show the EPR spectra of four of the glass samples which contain as network formers SiO_2 and P_2O_5, recorded after gamma irradiation with a radiation dose of 1.7 kGy.

The paramagnetic centres in silica glasses are characterized by g-factors which are greater than the g-factor of the free electron. It is assumed that the centres found in the glass samples are hole type centres. It is well known that the hole centres have a negative spin-orbit coupling constant and a g-factor which, usually, is very much larger than of the free electron [1]. According to literature [1] the line shape of the centre resonances is changed by the content of the modifier cations and hence by the non-bridging oxygens, too. Moreover, in alkali silicate glasses the type of alkali ions introduced in the silicate glass influences the line widths of the EPR signal.

The resonance line with a g value of 2.010 - 2.013 could be attributed to the HC_2 defect centre while the resonance line with a g value of 2.004 - 2.006 to the HC_1 centre [5,6,8,14]. As can be observed from the Figure 1, the contribution of the HC_1 to the intensity of the resonance line for the LYS sample is higher than the contribution of the same centre to the resonance line of the HY1.1 sample. The results suggest a higher concentration of Q^3 units in the LYS sample structure, which are supported by the ^{29}Si MAS-NMR results, reported elsewhere [15].

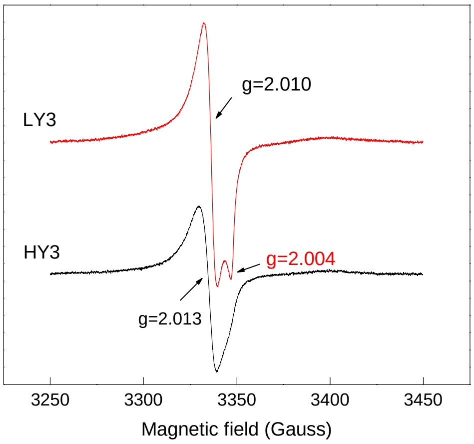

Fig. 1. EPR spectra for the HY1.1 and LYS samples irradiated with 1.7 kGy.

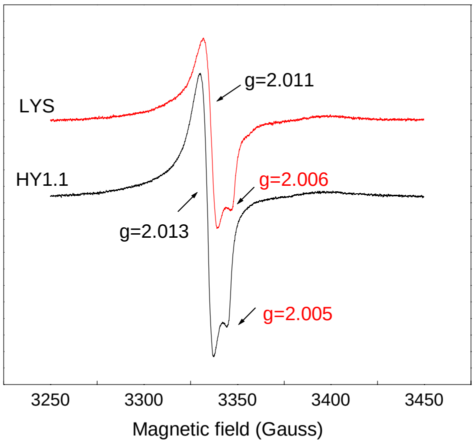

Fig. 2. EPR spectra for the HY3 and LY3 samples irradiated with 1.7 kGy.

The EPR spectrum of the HY3 sample (Fig. 2) show almost a single resonance line with g value of 2.013 corresponding to the HC_2 centre. However, the HC_1 centre is present in the glass structure but its contribution to the EPR spectrum is quite small. The EPR results show that Q^2 units are preponderant species in the structure of this sample. The EPR spectrum of LY3 sample clearly shows the contribution of the two paramagnetic centres HC_1 and HC_2 to the resonance line, but again the predominant contribution is from HC_2 centre, in agreement with the ^{29}Si MAS-NMR results which show that Q^3 units are predominant in this glass structure.

The HY1.1 and LYS samples contain also in their composition small amount of phosphorus. Phosphorus does not copolymerize with the silicate glass network for concentrations of few percent. It separates into regions rich in Q^0 and Q^1 species [16]. ^{31}P MAS-NMR spectra HY1.1 and LYS sample show the presence of Q^0 units in the glass structure [15]. No centers related to this element could be identified as induced by gamma irradiation [17,18]. Moreover, defect centres related to yttrium were not induced in the glass structure by gamma irradiation [19].

The EPR spectra of two glass samples HY2 and HY4 which contain boron oxide in their composition are shown in Fig. 3.

As can be observed from the Figure 3 the EPR spectra for the samples with boron content are split into four resonance lines.

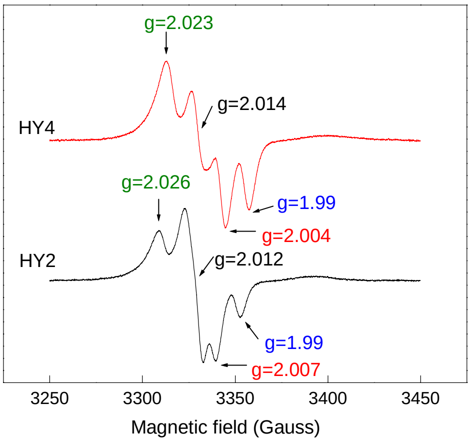

Fig. 3. EPR spectra for the HY2 and HY4 samples irradiated with 1.7 kGy.

The line with a g value of 2.012 - 2.014 could be attributed to the HC_2 centre and the line with a g value of 2.004 - 2.007 to the HC_1 centre, related to the SiO_4 tetrahedral units with one or two non-bridging oxygen. For HY2 sample, HC_2 centre has the main contribution to the EPR resonance line. ^{29}Si MAS-NMR results on this sample show that Q^2 units are preponderant in its structure. On the contrary, for the HY4 sample Q^3 species are the main structural units. The EPR spectrum of HY4 sample reveals a high contribution of the HC_1 centre to the resonance line. The resonance line with g value of 1.99 corresponds to the boron electron centre, E'. The presence of the resonance line with g value of 2.023 indicates the presence of a new centre in the glass structure. According to literature this centre is a boron oxygen hole centre (BOHC), which consist of a hole trapped by non-bridging oxygen atom in trigonal boron unit. The BOHC are usually present in the borosilicate and borophosphosilicate glasses [2,20-24]. These defect centres present in the glass samples are superimposed and are not clearly distinguishable. As can be observed from the spectra, the contribution of the boron centres to the resonance line of the HY4 sample is higher than for HY2 sample. This is due to the greater amount of boron oxide entering the HY4 composition than the HY2 composition.

3.2. EPR study of sol-gel non-crystalline microspheres

The as-prepared samples by sol-gel and spray-drying methods do not exhibit paramagnetic centres as the heat treated samples. It is known that the paramagnetic state generating the signal of the dried gel prepared by sol-gel method is trapped in pores of the gels. The pore geometry is unaltered if the thermal treatment is not applied. This could explain the absence of the signal in the non-thermal treated samples. However, by heat treatments at higher temperature (above 500 °C) the porosity collapses and strain in the sample leads to fracture of Si-O-Si [4].

The EPR spectra of the thermally heated samples at 700 °C are illustrated in Figs. 4 and 5. Since the starting solutions were $Si(OC_2H_5)_4$, H_2O and HCl the formation of oxygen radicals is expected. The g-values of carbon and nitrogen related radicals reported in literature [25] are not observed in the investigated samples.

The EPR spectra show the presence of a resonance line with $g_1 = 2.004$, $g_2 = 2.008$ and $g_3 = 2.021$, which could be attributed to the NBOHC (Figs. 4 and 5). Moreover, a resonance line with $g_4 = 2.043$ can be observed in the recorded spectra, which indicates the presence of a second paramagnetic centre in the sample structure, O_2^- centre. Thus, it is appropriate to suggest that two types of defect centres, NBOHC and O_2^-, which are superimposed, are present in the structure of the thermal heated samples after gamma irradiation.

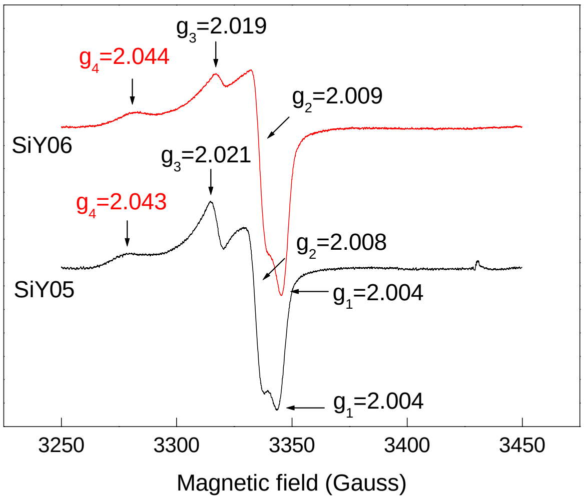

Fig. 4. EPR spectra of the SiY05 and SiY06 sample irradiated with 1.3 kGy.

As can be observed in the figures, there are differences between the EPR spectra of the SiY05 and SiY06 samples compared to the spectra of the SiY09 and SiY12 samples. The intensity of the signal corresponding to NBOHC centres for the SiY05 is higher than for the other samples suggesting a higher concentration of this type centre in the sample. This could be due to the presence of more strained three-membered rings in the sample network. It is assumed that bond strain due to the small rings increases radiation sensitivity [12,13] and induces the oxygen hole centres. The results are supported by ^{29}Si MAS-NMR results which show that more Q^4 units are present in the structure of SiY05 and SiY06 samples than in the structure of SiY09 and SiY12 samples. As a consequence, more Si-O-Si bonds are present in the structure of SiY05 and SiY06 samples which could be precursor of the NBOHC.

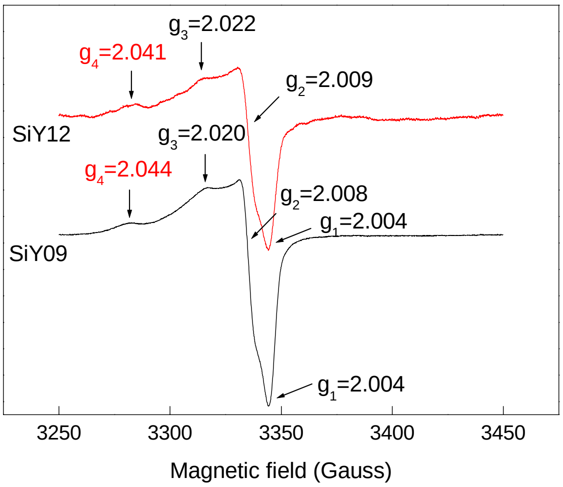

Fig. 5. EPR spectra of the SiY09 and SiY12 samples irradiated with 1.3 kGy.

On the contrary, the O_2^- centres are preponderant paramagnetic centres in the structure of the SiY09 and SiY12 sample. This could be explained by the presence of more silanols groups which are the precursors of these centres, due to the high H_2O/TEOS ratio used for the preparation of these samples. Moreover, the ^{29}Si MAS-NMR results indicate the presence of higher amount of Q^3 units in the structure of these samples than for the SiY05 and SiY06 samples. As a consequence more amount of Si-OH bonds are present in the structure of the SiY09 and SiY12 samples.

4. Conclusions

The paramagnetic centres induced after exposure to gamma radiation were used for characterization of the local structure of the investigated materials by EPR spectroscopy.

Two types of paramagnetic centres, HC_1 and HC_2 are induced by gamma irradiation of the melt-derived glass samples, which are related to the presence of the SiO_4 units with one or two non-bridging oxygen atoms. In the borosilicate glass samples, two additional centres related to the presence of boron in their composition are induced by gamma irradiation. These defect centres are boron electron centre (E') and boron oxygen hole centre (BOHC).

After gamma exposure of the sol-gel microspheres, oxygen hole centres (NBOHC) and O_2^- centres were evidenced by EPR spectroscopy. The concentration of these defect paramagnetic centres depends on the sol chemistry and thermal history. Strained three-membered rings are precursors to oxygen hole centres (NBOHC) and Si-OH groups for the O_2^- centres.

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