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Low dose gamma irradiation effect on aluminosilicate compounds

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Iron and rare earths containing aluminosilicate systems, that may be further considered for biomedical applications, were obtained following the sol-gel route. After drying, the samples were heat-treated at 500°C or 1200°C. Because the sterilisation of such biomedical compounds is usually realized with gamma rays, the samples were gamma irradiated and investigated with respect to possible occurrence of nocuous irradiation effects. Electron paramagnetic resonance (EPR) spectroscopy was used to characterize paramagnetic centres occurring in the gamma ray irradiated samples. The EPR studies demonstrate that various radiation-induced defects, like surface defects and peroxy centres, are present in the analysed systems. A higher concentration of defects was detected for samples treated at 500°C, as compared to samples treated at 1200°C. EPR silent defects induced during sample preparation, and evidenced after gamma rays exposure, can be removed by thermal treatment applied at high temperatures.

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1. Introduction

Glass systems are very often used as bone repairing and substituting materials in many dental and orthopaedic applications due to their excellent biocompatibility and osteointegration [1]. Aluminosilicate systems containing radioactivable isotopes like yttrium, dysprosium, holmium, samarium or rhenium are of interest for in situ radiotherapy [2-4]. The therapeutic effects in cancer treatment are considerably enhanced when two methods, e.g. radiotherapy and hyperthermia, are simultaneously applied [5]. The addition of iron to aluminosilicate systems containing radioactivable isotopes can introduce a ferrimagnetic phase proper for local heating by magnetic hysteresis [6, 7].

There is great interest in studying these systems with respect to structure-properties correlation and effects of different external agents like temperature, nuclear radiations, chemical agents and mechanical stress on the physical-chemical caracteristics [1, 4, 8]. At the same time, it is necessary to investigate the effects that could occur during the sterilization, because all biomaterials must be sterilised after fabrication and prior to their use, in order to reduce the risk of infections and associated complications [9, 10]. Despite the availability of a wide range of sterilisation techniques, it is generally agreed that no single sterilisation process is capable of sterilising without adverse effects, all processes having their own advantages and disadvantages [11-13]. Gamma irradiation is one of the most efficient sterilisation method. Prevoius studies shown that a minimum dose of 25 kGy would be reasonable inclusively for microbiological sterilisation [14], but lower doses can be considered for inorganic systems which do not require microbiological sterilisation. This method is a very easy, rapid and efficient, but as every sterilization method, has its own inconvenient. Ionising radiation can generate electrons and holes in the materials leaving radicals or defects. Non-bridging oxygen (NBO) atoms are quite common in SiO_2 films that are not oxygen-deficient. An NBO can trap holes and thus it is referred to as an oxygen-hole center (OHC) [15, 16]. The non-bridging oxygen hole center (NBOHC, ≡ Si−O•) is commonly observed in SiO_2 after light irradiation, as detected by Electron Paramagnetic Resonance (EPR).

A commonly-encountered oxygen-related point defect is the E' center, ≡Si•, which is defined as a relaxed oxygen vacancy in SiO_2 and is usually negatively charged. Here, the E' center constitutes a trivalent Si atom that has an unpaired electron in a dangling orbital and is back-bonded to three oxygen atoms. The E' center is perhaps the most commonly observed defect in irradiated thin films of SiO_2 [16]. The displaced interstitial oxygens by non-radiative decay of self-trapped excitons can form O_2 molecules and react with the E' center to generate a peroxy radical (PR, ≡ Si−O−O•). A self-trapped hole (STH), in the form of ≡Si-O•-Si≡, is considered to be one of the most fundamental point defects in SiO_2. Radiation can generate STH by trapping a hole at an unperturbed site [17]. A promising technique that can be used to describe and explain the radiation-induced paramagnetic centres is the Electron Paramagnetic Resonance (EPR), an effective technique used to characterise the local structure of crystalline or vitreous materials.

This article briefly describes the effects of low dose gamma irradiation for sterilisation purpose on aluminosilicate compounds of biomedical interest. Results concerning paramagnetic irradiation defect centres that were produced at room temperature in sol-gel derived

aluminosilicates containing rare earth (yttrium or dysprosium) and iron are reported.

2. Materials and methods

The sol-gel method, via hydrolysis and condensation of molecular precursors, was used to prepare the samples, because this approach is a high-purity process an leads to an excellent sample homogeneity. The composition of the investigated aluminosilicate systems is given in Table 1. The compounds were synthesized using as starting materials silicic acid ($Si(OH)_4$), aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) and dysprosium nitrate ($Dy(NO_3)_3 \cdot H_2O$) with high grade of purity. After the gel formation, the samples were filtrated, dried at 110ºC for 2 hours and then, according to thermal analysis results [18], they were heat-treated at 500°C and 1200°C for one hour and 24 hours, respectively.

Table 1. Samples composition.

Code	Components (mol %)				
	SiO_2	Al_2O_3	Fe_2O_3	Dy_2O_3	Y_2O_3
S1	60	20	20		
S2	60	20	10	10	
S3	60	20	10		10

The structure of the prepared aluminosilicates compounds was investigated before and after applied thermal treatment by X-ray Diffraction (XRD). The X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer using CuK_α radiation (λ=1.54 Å).

The samples were exposed to gamma rays for a few weeks, using a ^{60}Co source with a debit dose of 10 Gy/h. The irradiation dose was close to 8 kGy.

The Fourier Transform Infrared (FTIR) spectroscopic measurements were performed, before and after gamma exposure, by means of attenuated total reflectance using Equinox 55 Bruker instrument with a resolution of 2 cm^{-1}.

Electron resonance spectra of non-irradiated and gamma-irradiated samples were recorded by an EPR spectrometer, ADANI type, operating at 9.4 GHz (X band). The magnetic field was modulated at 100 KHz and the spectra were displayed as the first derivate of the absorption curve. All spectra were recorded at room temperature.

3. Results and discussion

The X-ray diffraction pattern of the dried samples reveals no crystalline peaks. The patterns consist of only a large waved line denoting a disordered structure. After the heat treatment applied at 500°C, the XRD patterns do not evidence any structural changes for the samples containing beside 10 mol % Fe_2O_3 also 10 mol % Y_2O_3 or Dy_2O_3, but for the sample with 20 mol % Fe_2O_3 (Fig. 1b) weak crystalline peaks are recorded, that indicate the presence of poorly crystallized hematite particles in this sample. For the 1200°C heat treated sample both tridymite (SiO_2), aluminosilicate of mulite ($Al_6Si_2O_{13}$) type, hematite and magnetite crystals are identified (Fig. 1c). The mulite structure confers to sample a high structural stability.

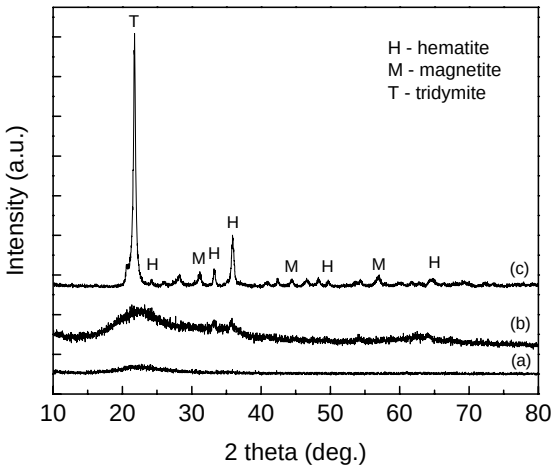

Fig.1. XRD patterns of samples with 20 mol% Fe_2O_3 before (a) and after heat-treatment at 500°C (b) and 1200°C (c).

FTIR analysis using KBr disk technique does not show spectroscopic changes for these samples when they are subject to gamma radiation (Fig. 2). The FTIR spectra reveal only the bands corresponding to different vibration of Si-O-Si and Al-O-Al bonds [19].

EPR is the method used to investigate the irradiation defect centres, which generally occur in the ppm range and cannot be easily evidenced with other methods. The trapped electron and hole centres are sometimes paramagnetic (as free radicals) and give rise to EPR signals [20]. Physical properties of the glasses can change when they are subject to ionising radiation. The kind and the extend of the properties change depend on the kind of radiation and also on the composition of the glasses. The results of exposure to ionising radiation such as neutrons, protons, energetic electrons, gamma rays, X-rays or sometimes even UV-light is the generation of defect centres. These defect centres may comprise, for example vacancies and interstitials in an otherwise random network. Such displaced atomic species may be created by 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 [21].

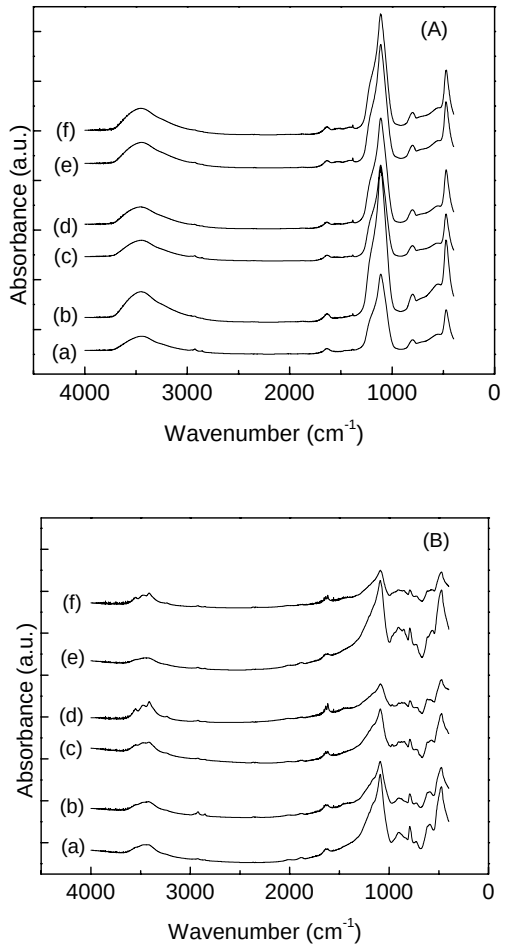

Fig. 2. FTIR spectra recorded from aluminosilicate compounds heat-treated at 500°C (A) and 1200°C (B) before (a, c, e) and after (b, d, f) gamma ray exposure.

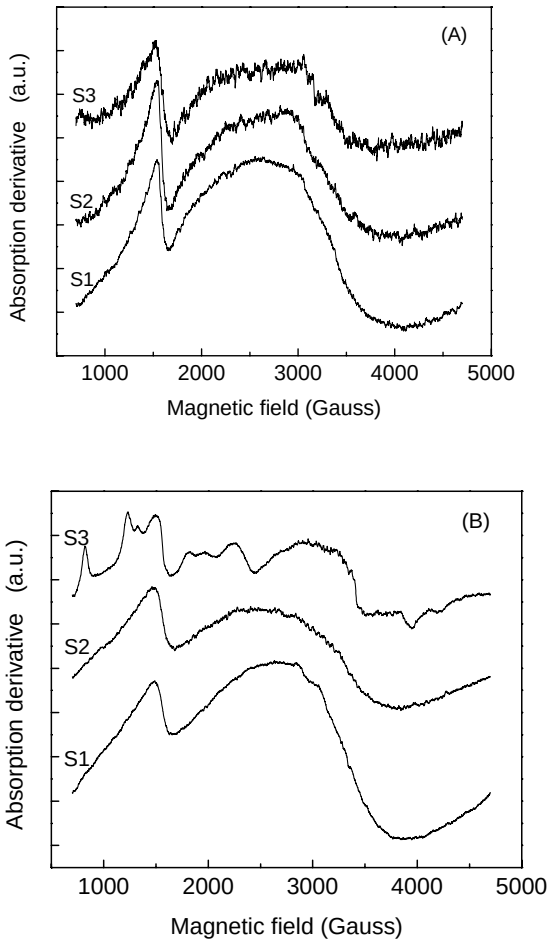

Fig. 3. First derivative EPR spectra of aluminosilicate compounds heat-treated at 500°C (A) and 1200 °C (B) before gamma exposure.

The paramagnetic centres in silica glasses are characterised by g-factors which are greater than the g-factor of the free electron. It is assumed that the centres found in silicate glass are hole type centres. It is well known that the hole centres have a negative spin-orbit coupling constant and a g-factor factor which, usually, is larger than the free electron [22].

The most frequently identified intrinsic point defects that are induced by radiation in SiO_2 include oxygen vacancy species such as NBOHCs (≡ Si−O•), E' centers (≡ Si•) peroxy radicals (≡ Si−O−O•) and self-trapped holes (≡ Si −O• −Si ≡) [16, 23, 24].

The X-band EPR spectra of glasses with Fe^{3+} ions usually exhibit two well defined lines at $g_{eff} \sim 4.3$ corresponding to the isolated Fe^{3+} ion and at $g_{eff} \sim 2$ attributed to the Fe^{3+} species that participate to dipole-dipole interactions (Fig. 3). In silicate glasses the $g_{eff} \sim 2$ line is often present even at very low Fe_2O_3 content [25-27]. The $g_{eff} \sim 4.3$ resonance line has been assigned to tetracoordinated Fe^{3+} by various investigation [25] and to orthorhombic distortion of both tetrahedral and octacoordinated Fe^{3+} by others [16]. Additional signals occurring from paramagnetic defects were detected mainly for 110°C dried and 500°C heat-treated samples (Fig. 4).

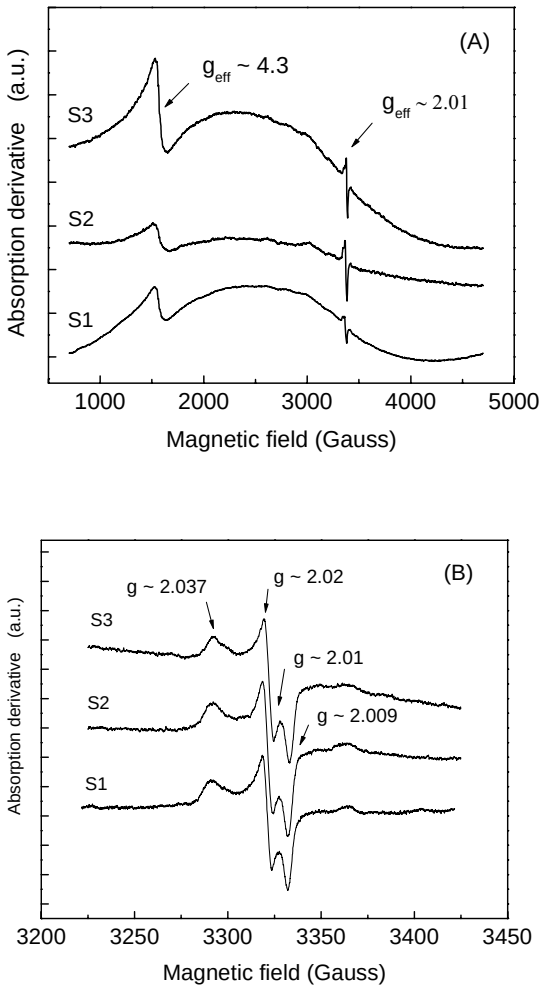

Fig. 4. First derivative EPR spectra of aluminosilicate compounds heat-treated at 500°C, using a sweep width of 4000 G (A) and 200 G (B).

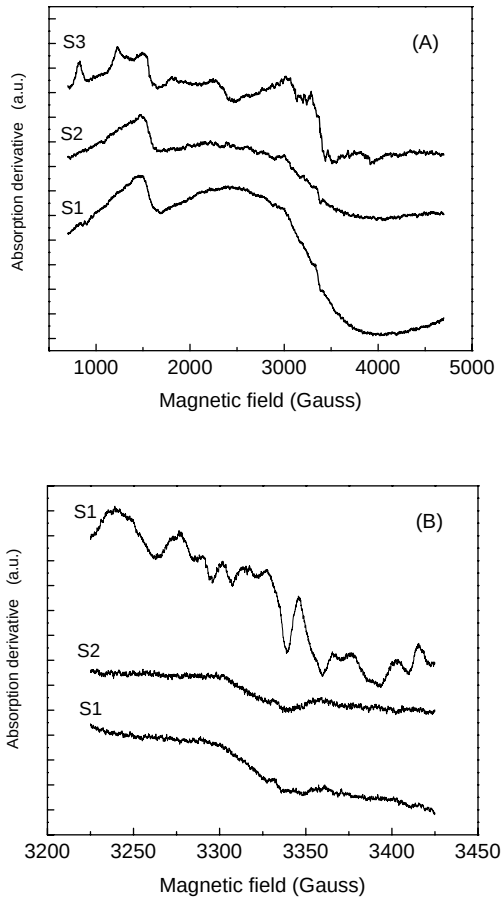

Fig. 5. First derivative EPR spectra of aluminosilicate compounds heat-treated at 1200°C, using a sweep width of 4000 G (A) and 200 G (B).

For the crystallised samples resulted after the heat-treated applied at 1200°C (Fig. 5) the EPR spectra reveal a very weak signal at g_{eff} ~ 2.01 due to a low number of lattice defects associated with oxygen or cation vacancies, that denotes a very good stability of the crystalline compounds. The analysis indicates that for the samples treated at 500°C the defects concentration is meaningful greater than for the samples treated at 1200°C which is in very good agreement with the idea that thermal treatment can restore the material structure, and the native defect centres are almost vanished.

Regarding the g factors of the resonance line recorded from the samples heat-treated at 500°C, the presence of resonance line with g ~ 2.037 indicates the presence of paramagnetic peroxy centres, OHC (g ~ 2.037). The resonance line with g ~ 2.02; g ~ 2.0179; g ~ 2. 009 can be assumed to NBOHC (Fig. 3 (B)). E' centres cannot be detected by EPR at room temperature because of saturation process even at very low power microwaves (0.01 mW) [14]. For the samples treated at 1200°C the radiation induced defects cannot be showed by EPR, explaining the very good stability of the crystalline compounds. EPR silent defects induced during sample preparation, and evidenced after gamma rays exposure, can be relieved by thermal treatment applied at high temperatures.

4. Conclusions

After gamma exposure of the sol-gel prepared aluminosilicate samples, oxygen hole centres and peroxy centres were evidenced by EPR spectroscopy. The concentration of these paramagnetic centres depends on the sol chemistry and thermal history. It was evidenced that the paramagnetic defects characterised by EPR may be created during preparation and are induced by gamma exposure, but they disappear while the temperature of the thermal treatment increases. In the samples treated at 500°C the defects concentration is meaningful greater than in those treated at 1200°C, denoting that the greater the crystallisation degree the better the stability of the irradiated samples against the occurrence of structural defects.

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