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Structural and magnetic properties of CaO-P_2O_5-SiO_2-Fe_2O_3 glass-ceramics for hyperthermia

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Abstract

Calcium–silica–phosphate glasses containing iron were partially crystallised to obtain a glass-ceramic system, applicable in hyperthermia treatments. The increasing iron content determines a higher glass transition temperature and the disposal of iron ions in small clusters. The magnetisation values for vitroceramic samples suggest that the main contribution to magnetisation is due to iron ions from magnetite.

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1. Introduction

Hyperthermia for treatment of tumours may be induced in tissue by applying an alternating magnetic field to a region implanted with magnetic materials. Small magnetic particles or spheres deposited in tissue will cause heating through hysteresis losses. Experimental data [1] demonstrated that glass-ceramic-mediated hysteresis heating may be a useful therapeutic approach in the treatment of cancer which offers the advantage of producing a highly localised and predictable tumour volume hyperthermia [2]. The use of calcium phosphate glasses and glass-ceramics as bone substitutes has become common in orthopaedic surgery. Ferrimagnetic calcium phosphate glass-ceramics are successfully applied to reinforce the bone and to decrease the recurrence of tumours by hyperthermia treatment [3–5]. In these samples, the development of ferrimagnetic crystallites in iron rich phases is essential.

The aim of this paper is to show the structural effects caused by iron addition to calcium–silica–

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phosphate glasses and to study the vicinity and magnetic interactions of iron ions of CaO–P_2O_5–SiO_2–Fe_2O_3 glass and glass-ceramic samples.

2. Experimental

Glass samples belonging to the quaternary $x\mathrm{Fe_2O_3} \cdot 45(3.34\mathrm{CaO} \cdot \mathrm{P_2O_5})(55-x)\mathrm{SiO_2}$ system ($0 \leqslant x \leqslant 30$ mol%) were prepared using SiO_2, $CaHPO_4 \cdot 2H_2O$, $CaCO_3$ and Fe_2O_3 as starting materials of reagent grade purity. The samples were obtained by quickly undercooling at room temperature of mixed row materials melted at 1500 °C in corundum crucibles. Specimens of the glass samples were heated for 30 min at 1000, 1100 and 1200 °C in air and then were slowly cooled down in the furnace to room temperature.

Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analyse (DTA) curves were carried out with a heating rate of 10 °C/min using a MOM derivatograph (MOM, Hungary). The electron paramagnetic resonance (EPR) spectra were recorded on powder samples with a Bruker ESP-300 EPR spectrometer, in X band, at room temperature. The magnetisation measurements were carried out in the temperature range 80–850 K using a Curie–Weiss balance. The field dependence of magnetisation was determined on self-made equipment by using the extraction method.

3. Results and discussion

In $x\mathrm{Fe_2O_3} \cdot 45(3.34\mathrm{CaO} \cdot \mathrm{P_2O_5})(55-x)\mathrm{SiO_2}$ system, both SiO_2 and P_2O_5 are glass formers while CaO and Fe_2O_3 act as glass network modifiers. The structural evolution of glass samples in function of composition was first checked by determining the glass transition and crystallisation temperatures from DTA. The data show that the glass transition temperature increases by addition of iron up to 20 mol% (Fig. 1). The lack of endothermic events from the DTA curves, at least up to 1000 °C, proves at the same time [6,7] the stability of the crystalline phases developed in these samples [8].

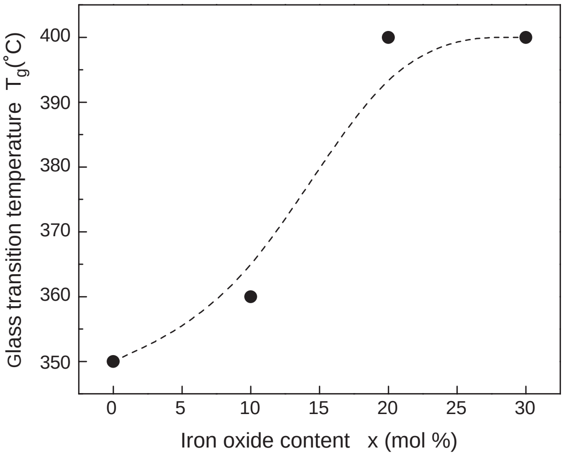

Fig. 1. Composition dependence of glass transition temperature.

The electron paramagnetic resonance spectra of the investigated samples consists of a large and relatively symmetric line. This feature is specific to disordered oxide systems with high Fe_2O_3 content wherein spherical magnetic monodomain particles are formed [9], most probably magnetite particles. The resonance line at $g \approx 2.0$ is shifted to lower values of the magnetic field when the iron oxide content increases (Fig. 2). This result could be assigned to the occurrence of magnetic clusters in the samples with higher Fe_2O_3 content. The size of these clusters and the local order are influenced by the heat treatment applied up to 1200 °C. The spectrum of the heat-treated sample contains besides the line typical of untreated glass sample, an additional narrow line arising from Fe^{3+} ions disposed in the crystalline phases well developed during the applied heat treatment. The crystalline phases containing iron were identified by X-ray diffraction as being in majority F_3O_4 and small amounts of α-Fe_2O_3 and γ-Fe_2O_3 [8].

The magnetisation measurements in function of magnetic field indicate ferrimagnetic behaviour of the investigated samples. The saturation magnetisation is about 8 Gs cm^3/g and starts around 2.5 kOe for the glass-ceramic obtained after heat treatment at 1100 °C (Fig. 3). The temperature dependence of the magnetisation measured in a magnetic field of 7.8 kOe (Fig. 4) confirms, for the same sample, the value of saturation

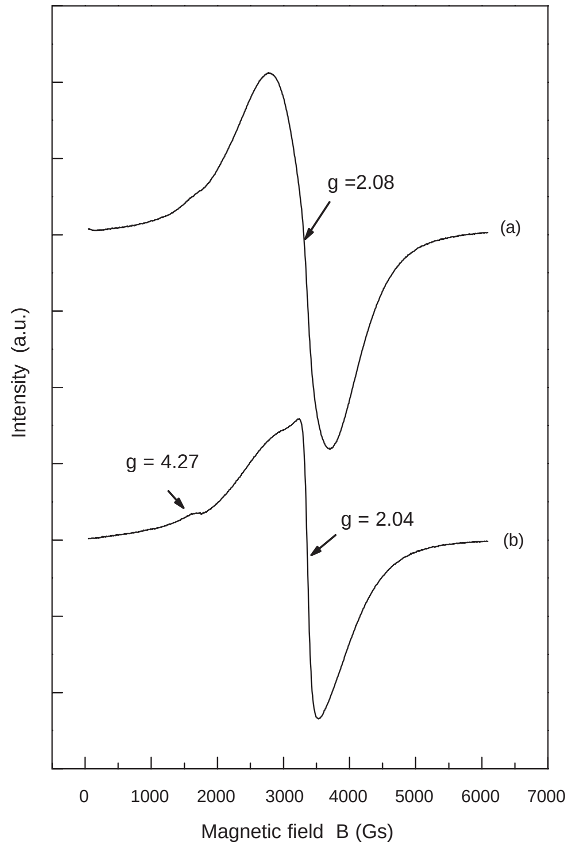

Fig. 2. EPR spectra of glass and glass ceramic samples containing 10 mol% Fe_2O_3.

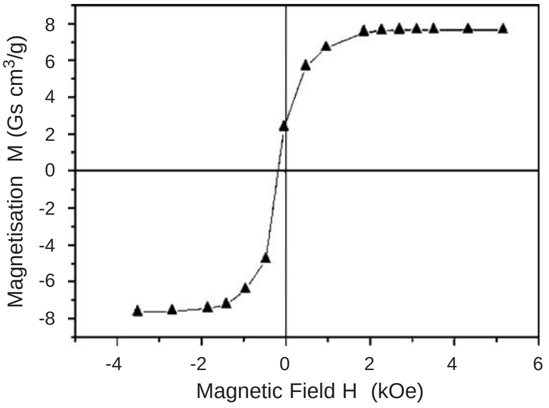

Fig. 3. Field dependence of magnetisation for $10Fe_2O_3 \cdot 45SiO_2 \cdot 45(3.34CaO \cdot P_2O_5)$ sample after heat treatment at 1100 °C.

magnetisation and shows the Curie temperature to be around 820 K. These values suggest that the main contributor to magnetisation are iron ions from magnetite Fe_3O_4, with an additional contribution from γ-Fe_2O_3 (maghemite) [10]. Indeed these crystalline phases were evidenced by XRD analyses. The Curie temperature, T_c, and the saturation magnetisation of the mass unit, $\sigma_s = M_s/m$, for different iron oxides [11] are given in Table 1.

The magnetic moment per unit formula is 3.9 μ_B, as determined from the saturation magnetisation in value of 7.5 uem/g Gs (Fig. 3) and taking into account the Fe_2O_3 content [12] introduced in the precursor glass sample. The value of 7.8 uem/g Gs for the saturation magnetisation determined by extrapolation at 0 K (Fig. 4) leads to a magnetic moment per unit formula of 4.05 μ_B. These values obtained from different

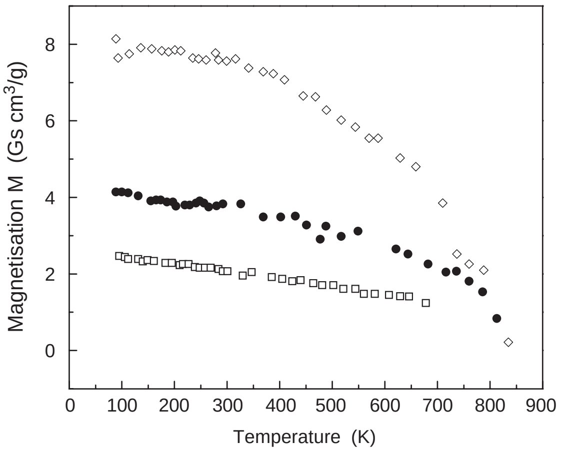

Fig. 4. Temperature dependence of magnetisation for $10Fe_2O_3 \cdot 45SiO_2 \cdot 45(3.34CaO \cdot P_2O_5)$ samples after heat treatment at 1000 °C (□), 1100 °C (◇) and 1200 °C(•).

Table 1
Characteristic magnetic values for iron oxides

Compound	Magnetic behaviour type	T_c (°C)	σ_s (Am^2/kg)
Fe_3O_4	Collinear ferrimagnetism	575–585	90–92
α-Fe_2O_3	Canted antiferomagnetism	675	0.4
γ-Fe_2O_3	Collinear ferrimagnetism	600	80

measurements carried out on different pieces of sample prove the sample homogeneity and data reproducibility.

At the same time, the results show that due to the applied heat treatment in the glass-ceramic sample, the iron oxide is preponderantly crystallized as Fe_3O_4, but also α-Fe_2O_3 and γ-Fe_2O_3 occur. On remarks (Table 1) that α-Fe_2O_3 has a very low saturation magnetisation ($0.4\,Am^2/kg$) as compared with Fe_3O_4 (90–$92\,Am^2/kg$), while the saturation magnetisation of γ-Fe_2O_3 ($80\,Am^2/kg$) is close to that of magnetite, so that the substitution of the last two ones does not significantly influence the saturation magnetisation and implicitly the magnetic moment per formula unit.

4. Conclusions

In the investigated CaO–P_2O_5–SiO_2–Fe_2O_3 glass system, with Ca/P ratio similar to hydroxyapatite, the addition up to 30 mol% of iron oxide on the account of silica determines an increase of the precursor glass stability. After heat treatment, the iron preponderantly crystallises as magnetite, but hematite and maghemite are also developed. According to the EPR results, the iron ions seem to form low-sized magnetic domains even in glass samples. The magnetisation measurements in function of magnetic field and temperature indicate a ferrimagnetic behaviour with the Curie temperature around 820 K for the investigated samples.

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