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Understanding the magnetic behavior of heat treated $CaO–P_2O_5–Na_2O–Fe_2O_3–SiO_2$ bioactive glass using electron paramagnetic resonance studies

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ABSTRACT

Bioactive glass of composition $41CaO–44SiO_2–4P_2O_5–8Fe_2O_3–3Na_2O$ has been heat treated in the temperature (T_A) range of 750–1150 °C for time periods (t_A) ranging from 1 h to 3 h to yield magnetic bioactive glass ceramics (MBCs). X-ray diffraction studies indicate the presence of bone mineral (hydroxyapatite and wollastonite) and magnetic (magnetite and α-hematite) phases in nanocrystalline form in the MBCs. Electron paramagnetic resonance (EPR) study was carried out to understand the variation in saturation magnetization and coercivity of the MBCs with T_A and t_A. These studies reveal the nature and amount of iron ions present in the MBCs and their interaction in the glassy oxide matrix as a function of annealing parameters. The deterioration in the magnetic properties of the glass heat treated above 1050 °C is attributed to the crystallization of the non-magnetic α-hematite phase. These results are expected to be useful in the application of these MBCs as thermoseeds in hyperthermia treatment of cancer.

1. Introduction

Bioactive glass and magnetic bioactive glass ceramics (MBCs) have been subjects of intensive study due to their biomedical applications. MBCs derived from bioactive glass compositions containing magnetic oxide(s) can be used as thermoseeds in hyperthermia treatment of cancer. This treatment is based on the observation that cancerous tissues are destroyed when heated to about 43 °C, while normal (healthy) tissues are capable of withstanding temperatures up to 46 °C [1, 2]. The magnetic phase present in the thermoseed generates and dissipates heat under an applied alternating magnetic field [3]. Magnetic properties of MBCs can be controlled by varying parameters such as size and shape of particles, chemical composition, surface morphology, interaction of magnetic ions in the glassy matrix, etc. Knowledge of the distribution of iron ions and the crystallization process of various magnetic phases in glassy matrix upon heat treatment are crucial for understanding the magnetic behavior of these MBCs. Attempts have been made to understand the crystallization mechanism in various glass and glass ceramic compositions with the help of electron paramagnetic resonance (EPR) spectra [4–6]. The sensitivity of EPR spectra to the iron ion state and the environment about the ions makes it an appropriate probe for understanding the unusual magnetic behavior of the MBC mentioned above. Hence, an attempt is made in this work to use structural and magnetic data along with EPR spectra of heat treated $41CaO–44SiO_2–4P_2O_5–8Fe_2O_3–3Na_2O$ glass to account for its peculiar magnetic behavior above 1050 °C.

2. Experimental details

Parent glass with a composition (in mole %) of $41CaO–44SiO_2–4P_2O_5–8Fe_2O_3–3Na_2O$ was prepared from high purity SiO_2, Fe_2O_3, Na_2CO_3, $CaCO_3$ and $NH_4(H_2PO_4)$. Appropriate amounts of the starting compounds were taken in a platinum crucible, calcined at 800 °C in air before melting the charge at 1550 °C. The melt was then poured on a copper plate at room temperature to form glass. As-quenched glass was then heat treated at different temperatures (T_A) ranging from 750 °C to 1150 °C for different annealing times (t_A) such as 1, 2 and 3 h in air to yield the MBC. Powder X-ray diffraction technique was used to identify and quantify the phases crystallized in the heat treated glasses. International Centre for Diffraction Data (ICDD) files PDF # 85-1436, PDF # 03-0800, PDF # 74-0566 and PDF # 84-0655 corresponding to magnetite, α-hematite, hydroxyapatite and wollastonite, respectively, were

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used for phase identification and matching of the X-ray diffraction (XRD) data of the heat treated glass. Magnetization measurements were performed using a vibrating sample magnetometer (VSM, Lakeshore model 7410). EPR absorption spectra were recorded at 300 K using a JEOL JES-FA200 spectrometer operating at 9.4 GHz with 100 kHz magnetic field modulation.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the glass heat treated at 750 °C and 1150 °C at three different t_A. The XRD patterns show the evolution of various crystalline phases with annealing time. The XRD patterns confirm the presence of three phases in this MBC – two bone mineral phases viz., hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and wollastonite [$CaSiO_3$], and one magnetic phase, viz., magnetite [Fe_3O_4] as the major crystalline phase in both the samples. α-Hematite [α-Fe_2O_3] appears as an additional phase in the XRD pattern of the glass heat treated at 1150 °C. The presence of the bone mineral phases confirms the biocompatible nature of the MBCs. Lack of any intense peak in the XRD pattern of glass annealed at 750 °C shows that nucleation and growth of phases have just been initiated at this temperature. Average crystallite size (d_{av}) of different nanocrystalline phases crystallized at temperature above 750 °C has been calculated using the Williamson–Hall relation [7] Fig. 2

$$\beta \cos\theta = \frac{k\lambda}{d_{av}} + 4\varepsilon \sin\theta \quad (1)$$

where β is the integral breadth (full width at half maximum) of diffraction peak, ε is the strain, $k\lambda/d_{av}$ is the size component where d_{av} is the average crystallite size, λ is wavelength used, k is the Scherrer constant (which is 0.9 for nearly spherical particles) and θ is the Bragg angle. d_{av} of all phases increased as T_A and t_A were increased. Variation of d_{av} of magnetite as a function of T_A and t_A is shown in Fig. 3(a). It depicts a gentle increase in d_{av} up to 1050 °C and a sharp increase beyond this T_A for all t_A.

Fig. 2 shows the isothermal magnetization (M–H) curves obtained for the MBCs as function of applied magnetic field (H). All the samples exhibit magnetic hysteresis with those heat treated at higher T_A showing a tendency for magnetic saturation

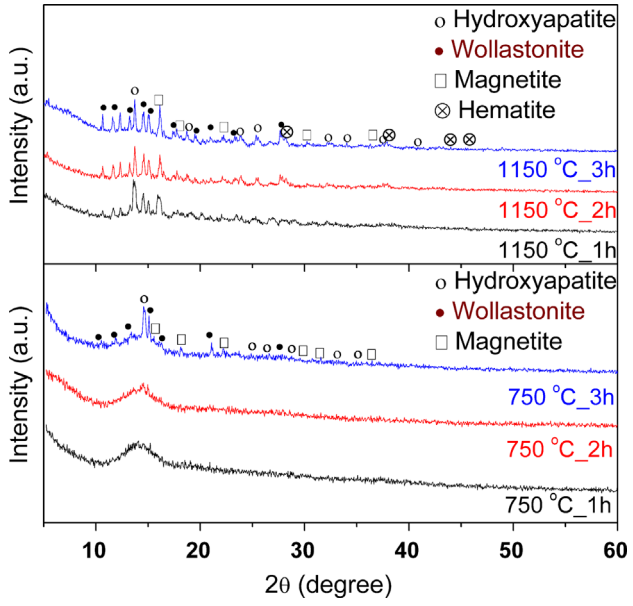

Fig. 1. Room temperature XRD patterns of MBCs at 750 °C and 1150 °C for different annealing time periods.

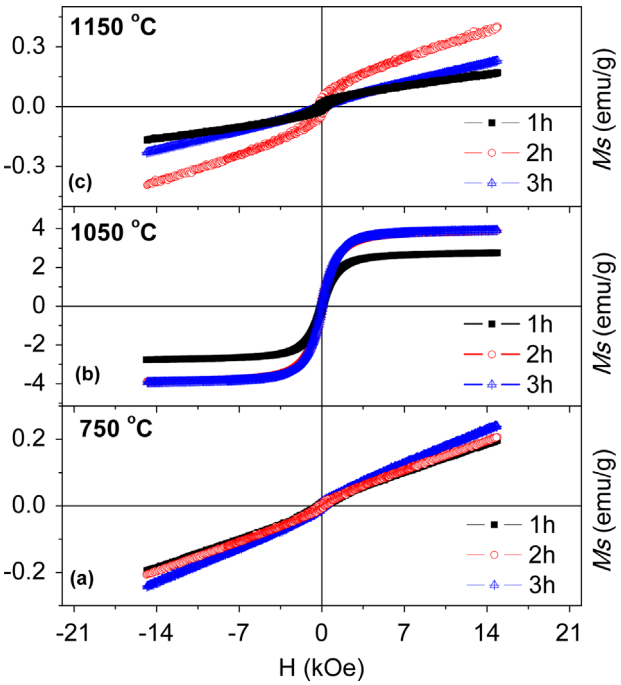

Fig. 2. VSM curves of glass annealed at (a) 750 °C, (b) 1050 °C and (c) 1150 °C for different time periods.

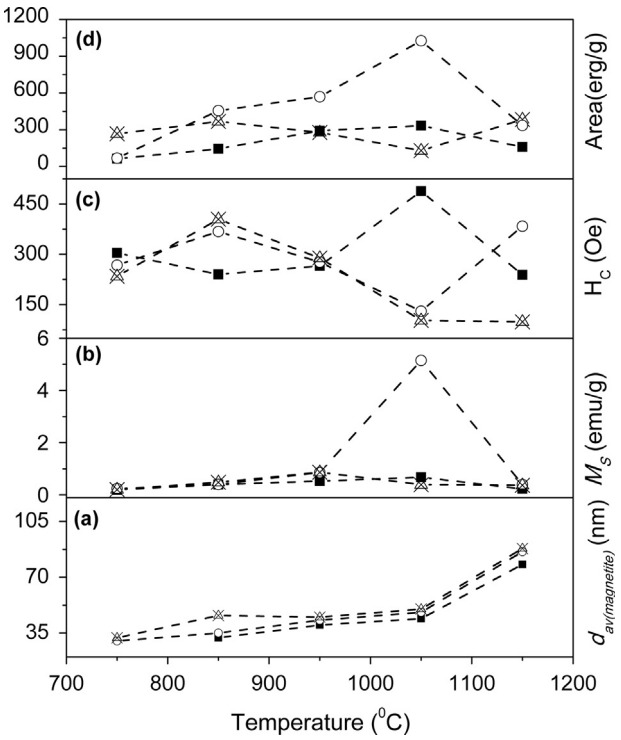

Fig. 3. Variation of (a) magnetite crystallite size, $d_{av(magnetite)}$, (b) saturation magnetization M_s, (c) coercive field H_c and (d) hysteresis loop area of MBCs as a function of annealing parameters T_A and t_A (symbols ■, ○ and Δ correspond to t_A of 1 h, 2 h and 3 h, respectively).

within 20 kOe. Saturation magnetization (M_s) of the samples increased with increasing T_A up to 2 h and deteriorated for $t_A > 2$ h. A random variation of coercivity (H_c) of magnetite crystallites in the glassy matrix has been observed. This behavior of H_c can be explained as follows. At low T_A, nucleation and crystallization of magnetite crystallites occur in a randomly distributed manner in the glassy matrix resulting in weak magnetic interaction. With increasing

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