

Structural properties of iron containing calcium-magnesium borophosphate glasses



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HIGHLIGHTS

- Structure and bioactivity of the $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5\text{-CaO-MgO-B}_2\text{O}_3$ system were studied.
- XRD, FTIR and ESR studies showed changes both in phosphate and iron environments.
- Bioactivity tests indicated that iron free sample showed some bioactivity.
- Crystallization tendency increased with increasing iron concentration.

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ABSTRACT

The glass system $x\text{Fe}_2\text{O}_3\cdot(55-x)\text{P}_2\text{O}_5\cdot 30\text{CaO}\cdot 5\text{MgO}\cdot 10\text{B}_2\text{O}_3$ has been prepared for $x=0\text{--}15$. Structural characterizations of as casted and heat treated samples were highlighted by means of X-ray diffraction, infrared and electron spin resonance spectroscopies. Effects of iron addition on the phosphate network have been identified by new bands observed in the $400\text{--}1150\text{ cm}^{-1}$ wavenumber range in the infrared spectra. Electron spin resonance spectra showed the iron ions ligand field effect through resonances centered at $g \approx 4.3$ and $g \approx 2.0$. There were discernable changes in the electron spin resonance spectra after the heat treatment. The samples were tested for bioactivity in simulated body fluids for 15 and 30 days. No evidence of bioactivity was found in the infrared spectra after 15 days immersion in simulated body fluid while three hydroxyapatite markers have been identified in the infrared spectrum of the iron free sample after 30 days immersion in simulated body fluid.

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Introduction

Double former glasses based on P_2O_5 and B_2O_3 with high modifier contents have been investigated in the last years for some new properties that could improve the bioactivity and high shock resistance [1,2]. Iron borophosphate glasses have been studied as a potential glass host for the vitrification of certain nuclear wastes [3]. The structural units that build the phosphate or borate vitreous structure, i.e. Q^3 , Q^2 , Q^1 , Q^0 tetrahedral units or BO_3 and/or BO_4 units have been highlighted by means of FTIR [4,5]. The exponent of the phosphate units (3–0) gives the number of bridging oxygen atoms which also indicates the depolymerization degree and the ability of the glass to link cations. Formation of mixed B–O–P linkages are possible in the glass structure illustrating interconnected vitreous network or independent borate or phosphate units bonded to

large vitreous structures [6,7]. When Fe_2O_3 is present in the composition, depending on its content and on the other constituents present, it can act as network modifier and/or as network former increasing the crosslink within the glass [8,9]. Iron ions can be present as FeO_4 (four coordinated) or FeO_6 (six coordinated) depending on the available oxygen atoms and can be in +2 or +3 valence state. The heat treatment upon the vitreous phosphate or borate glass network induces changes within the glass structure which may result in new properties and application areas. Besides the Mössbauer spectroscopy, electron spin resonance (ESR) is another important technique used to study the coordination of iron ions and interactions between magnetic ions. Addition of paramagnetic ions into the glass matrix introduces some changes in the vitreous state which affect the sites occupied by the ions and/or the valence state of the ions. It is hence necessary to study the glass structure and paramagnetic ion environment together to see this mutual effect.

Glass based materials are ideal mediums for medical applications because glass compositions can be tailored to obtain new glasses with desired properties. Such freedom in changing the

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composition allows phosphate based glasses to be suitable materials for the controlled release of therapeutic ions [10]. In these materials, P_2O_5 is a component that not only simulates bioactivity of the glass but also increases its biocompatibility by utilizing the body friendly oxides such as CaO and MgO [11]. Calcium is crucial in cell biology and calcium ions along with phosphate ions are the key components of the mineralized matrix that acts as a reservoir for calcium in the body [10]. Boron containing glasses, glass–ceramics and ceramics have been investigated as biomaterials, and effect of MgO on the glass network and its contribution to the bioactivity of calcium phosphate glasses have been studied [10].

The aim of this study consists of two parts: the first goal was to characterize the new glass system with composition $xFe_2O_3 \cdot (55 - x)P_2O_5 \cdot 30CaO \cdot 5MgO \cdot 10B_2O_3$ ($x = 0, 5, 10, 15$ mol%). Structural characterizations were done on as casted and heat treated glasses by XRD, FTIR and ESR. Heat treatment is one of the important methods to enlighten the structure of glasses as it is well known that there is a similarity in short range between glass and crystalline phase(s) that crystallizes from glass upon heat treatment. The second goal was to check the bioactivity of these samples in simulated body fluid (SBF) using FTIR spectroscopy.

Experimental

Glasses in the $xFe_2O_3 \cdot (55 - x)P_2O_5 \cdot 30CaO \cdot 5MgO \cdot 10B_2O_3$ ($x = 0, 5, 10, 15$ mol%) system were synthesized by melting the mixtures of reagent grade P_2O_5 , $CaCO_3$, H_3BO_3 , MgO and Fe_2O_3 using conventional melt quenching technique. The homogenized mixtures were melted in air in an electric furnace at 1250 °C for 15 min and the melts were quickly cooled to room temperature by pouring onto stainless-steel plates. All samples have been heat treated at 730 °C for 10 h.

Structures of the samples were investigated using a standard Bruker X D8 Advance powder diffractometer. The spectra were recorded on powdered samples in the $2\theta = 5-125^\circ$ range with steps of 0.01° .

Differential thermal analysis (DTA) measurements were performed using a Shimadzu DTG 60 model DTA spectrometer to determine the glass transition and crystallization temperatures of samples. Measurements were conducted in nitrogen atmosphere at a heating rate of $10^\circ C/min$ between 25 °C and 900 °C with Al_2O_3 as the reference medium.

FTIR absorption spectra were recorded at room temperature using a JASCO FTIR 4100 spectrometer. The measurements were done using the KBr pellet technique. In order to obtain good quality spectra, the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied each time to bulk glass to avoid structural modifications due to ambient moisture.

The ESR measurements of powder samples were carried out in the X-band (~ 9.79 GHz) at room temperature using a Bruker E-500 ELEXSYS spectrometer. To avoid the alteration of the glass structure due to the ambient conditions, especially humidity, samples were poured immediately after preparation and enclosed in tubular holders of the same caliber.

All the samples have been checked for bioactivity using Kokubo method in SBF which is a widely used method for preliminary bioactivity tests of materials [12]. Bioactivity tests were conducted for 15 and 30 days immersion times.

Results

XRD spectra of as casted and heat treated samples

XRD measurements were performed in order to check the glassy state of as quenched and heat treated samples, and the

patterns obtained are given in Fig. 1a and b. The heat treatment temperature was determined from the DTA measurements. The XRD patterns of as quenched samples given in Fig. 1a indicate that all four samples are amorphous while the XRD patterns of heat treated samples given in Fig. 1b show that samples containing $x = 10$ and 15 mol% Fe_2O_3 are more susceptible to structural changes during heat treatment. This proves the modifier action of iron ions which break the P–O bonds favoring the formation of new phosphate groups. For $0 \leq x \leq 5$, the XRD patterns contain one broad halo which demonstrates the amorphous nature of these samples. As the iron concentration is increased, sharp lines are observed in the XRD spectra indicating the existence of crystalline phase(s) in the glass matrix. Analysis of the XRD spectra revealed that the crystalline phases identified were $Fe_2P_4O_{12}$ (PDF # 78-2285), BPO_4 (PDF # 34-132) and $Ca_2P_2O_7$ (PDF # 03-0605), $Mg_2P_2O_7$ (22-1152), $Ca_3(PO_4)_2$ (PDF # 06-200), $B_{0.57}Fe_{0.43}PO_4$ (PDF # 50-210). The DTA measurements given in Fig. 2 revealed that iron free sample had no exothermic peak up to 800 °C while 5 mol% Fe_2O_3 containing sample showed a crystallization peak at 844 °C. On the other hand, the DTA spectra of $x = 10$ and $x = 15$ mol% Fe_2O_3 containing samples showed exothermic peaks

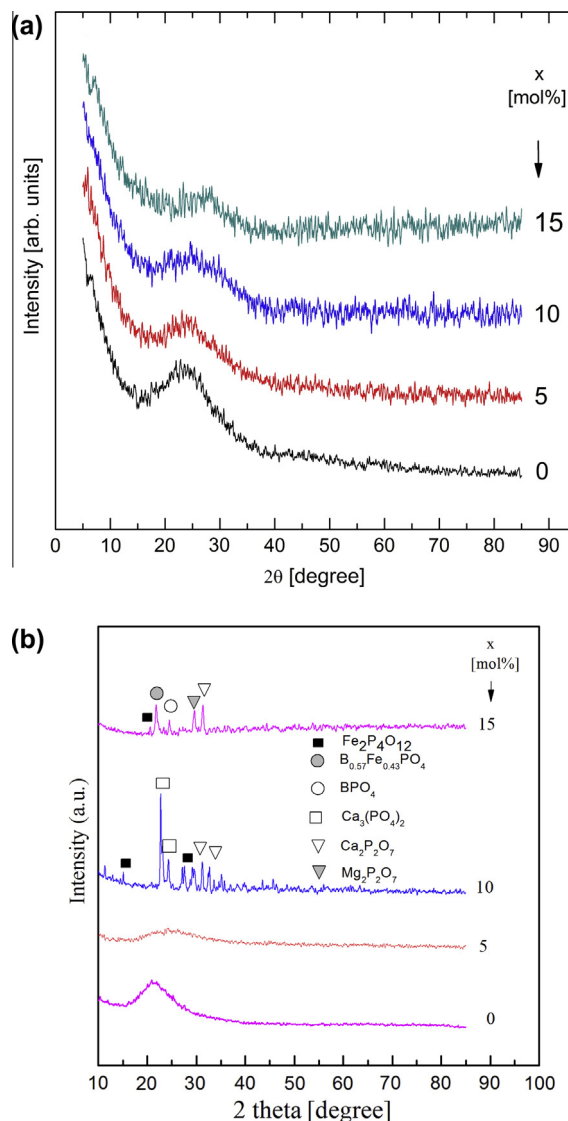


Fig. 1. XRD spectra of (a) as casted, (b) heat treated $xFe_2O_3 \cdot (55 - x)P_2O_5 \cdot 30CaO \cdot 5MgO \cdot 10B_2O_3$ system for $x = 0-15$.

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