Journal of Non-Crystalline Solids 361 (2013) 119–123

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Bioactive glass prepared by sol–gel emulsion

J.R.J. Delben [a,*], K. Pereira [a], S.L. Oliveira [a], L.D.S. Alencar [a], A.C. Hernandes [b], A.A.S.T. Delben [a]

[a] Centro de Ciências Exatas e Tecnologia, Universidade Federal de Mato Grosso do Sul, CP 549, 79070-900 Campo Grande, MS, Brazil
[b] Grupo de Crescimento de Cristais e Materiais Cerâmicos, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form 16 October 2012
Available online 25 November 2012

Keywords:
Bioactive glass;
Sol–gel emulsion

ABSTRACT

Bioactive glass (BG) particles with nominal composition $60SiO_2$–$36CaO$–$4P_2O_5$ (mol%) were prepared by the sol–gel emulsion method. The thermal parameters, morphology, and phase composition were characterized by means of thermal analysis, scanning electron microscopy, X-ray diffraction, and FT-IR absorption spectroscopy. The in vitro bioactivity of the samples was determined by immersing the samples in simulated body fluid. The findings indicated that the sol–gel emulsion method may be useful to prepare BG samples free of crystallization.

1. Introduction

Since 1969, bioactive glass (BG) ceramics prepared by melting with different compositions and, consequently, distinct physico-chemical features have been described in the literature [1]. The bioactivity of these glasses derives from their ability to be converted into apatite, which adheres well to living bones. To obtain bioactive glasses prepared by melting with reasonable adhesion to bones and negligible crystallization, a silica content below 60 (mol%) and high content of CaO, as well as a Ca/P molar ratio between 1 and 5 are required. However, it is a challenge to prepare glasses by melting in the CaO–P_2O_5 system with a molar ratio CaO/P_2O_5 higher than 1.2, since melting temperatures above 1500 °C are required [2]. Glasses and glass-ceramics with molar ratio CaO/P_2O_5 in the 1.2–2.0 range have been obtained only by using high contents of oxides such as SiO_2, Na_2O, MgO, TiO_2, ZrO_2, and SrO [3–5]; nevertheless, crystalline phases have been precipitated in the glass matrix, significantly reducing the bioactivity. Addition of CaF_2 to the oxide matrix lowered the crystallization temperature, slightly improved bioactivity [6], and provided a method for glass-ceramic production under controlled crystallization [7].

Silicate glasses prepared by sol–gel show promise for use as biomaterials, since the sol–gel method is able to provide highly pure and chemically homogeneous materials with a large surface area at low temperature [8]. Hybrid materials incorporating functional organic molecules can also be produced by sol–gel routes [9]. The reactivity of the glasses depends on both their porosity and the number of non-bridging oxygens (NBO) that can be controlled by the addition of cations such as Na^+, K^+, and Mg^{2+} which induce a breakdown of the glass network [10,11]. The sol–gel method also allows the preparation of bioactive glasses at low temperatures with SiO_2 concentration up to 90 mol% [12,13].

The sol–gel process, despite being very promising to produce BG samples, might lead to formation of unwanted glass-ceramic particles even when stabilized at temperatures below the crystallization temperature. This crystallization contributes to a reduction of the bioactivity of the material [14,15].

It has been a challenging task to develop wet routes able to produce crystallization-free bioactive glasses. Here we demonstrate that the sol–gel emulsion method can be used to synthesize BG samples with composition $60SiO_2$–$36CaO$–$4P_2O_5$ without crystallization. The influence of the heat treatment on the structural properties and phase composition of the bioactive glasses (BG) is also discussed.

2. Experimental

Bioactive glass samples with nominal composition $60SiO_2$–$36CaO$–$4P_2O_5$ (mol%) were prepared by the sol–gel emulsion method. Distilled and deionized water, nitric acid HNO_3 (QUIMEX, 65% BP), tetraethyl orthosilicate TEOS (Sigma-Aldrich 98% PA), ethyl alcohol (ISOF 95%), triethyl phosphate TEP (Sigma-Aldrich 99.8%) and calcium nitrate (Kinetic 99%) were used as precursors for the sol phase, as described elsewhere [13].

The sol–gel emulsion approach is based on two phases: an oil phase and an aqueous phase. The oil phase was formed from the surfactant Sorbitan Monooleate Span 80® (Fluka) diluted in filtered kerosene, while the aqueous phase consisted of distilled and deionized water as well as $NH_4{\cdot}OH$. The oil and aqueous phases were mixed under high-energy ultrasound to produce an emulsion. The sol was dripped under stirring and then centrifuged to separate the samples. Next, the particles were dried in an oven at 100 °C for 24 h. After the drying step, the sample was ground in an agate mortar and then annealed at 600 °C for 4 h in a furnace under ambient atmosphere.

* Corresponding author at: Centro de Ciências Exatas e Tecnologia, Universidade Federal de Mato Grosso do Sul, Cidade Universitária, s/n, CEP 79070-900, Caixa Postal 549, Campo Grande, MS, Brazil. Tel.: +55 67 3345 7036.
E-mail address: delbenbr@yahoo.com.br (J.R.J. Delben).

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http://dx.doi.org/10.1016/j.jnoncrysol.2012.10.025

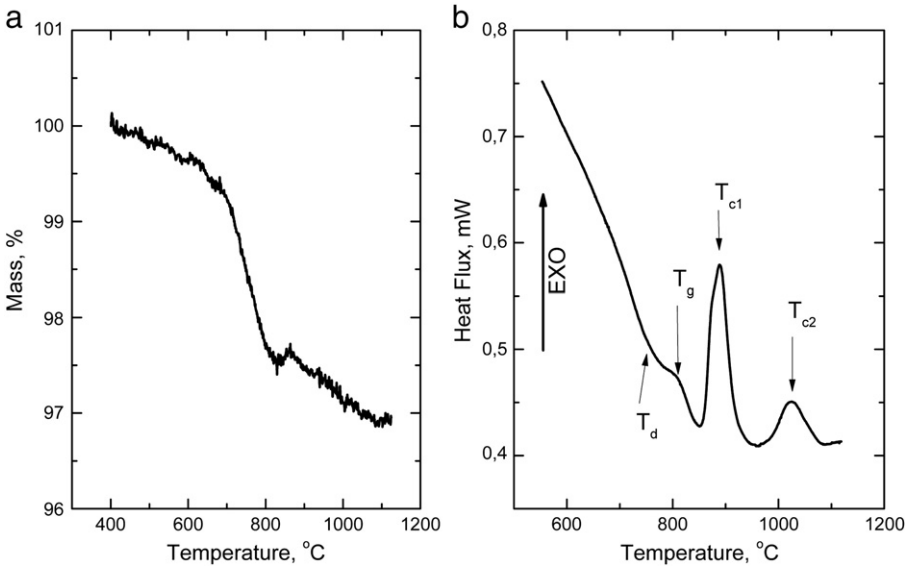

Fig. 1. (a) TG and (b) DSC curves of bioactive glass samples annealed at 600 °C.

This sample is henceforth termed E600. A portion of this sample was subsequently annealed at 750 °C for 2 h, hereafter termed E750.

The morphology was measured by scanning electron microscopy (SEM) (JEOL 6830LV Microscope). Crystalline and amorphous phases of the powders were determined by X-ray diffraction (XRD) using a Rigaku apparatus (Rotaflex RU200B) with CuK radiation operating at 50 kV and 100 mA. The XRD patterns were analyzed using the JCPDS data. Differential scanning calorimetry (DSC) and thermogravimetry (TG) curves were obtained in a Shimadzu TA-50 thermogravimeter using platinum crucibles and synthetic air. The vibrational groups in the samples were identified by a Fourier transform infrared spectroscopy FT-IR spectrophotometer (Perkin-Elmer Spectrum 100) with an Attenuated Total Reflectance (ATR) accessory.

Bioactivity was evaluated in vitro by immersing the samples in simulated body fluid (SBF), as described by Kokubo et al. [18]. Pellets of the particles were prepared and incubated at 37 °C for 4 and 10 days in about 50 mL of SBF. After each interval the samples were washed using distilled water, dried at 50 °C for 24 h, and then stored in a water-free container. Energy-dispersive X-ray spectroscopy (EDS) measurements were performed to evaluate changes in the relative contents of calcium and phosphorus in the samples submitted to the SBF.

3. Results and discussion

3.1. Thermal analysis

Fig. 1(a) shows the TG curve of the BG samples annealed at 600 °C. The TG curve indicates a continuous and smooth mass loss up to 680 °C, which may be attributed to the release of adsorbed water. Although decarbonation was observed in the 680–830 °C range, BG samples synthesized using the emulsion method lost less mass in this temperature range, indicating a low carbonate content in these particles.

The endothermic event (T_d) in the 680–830 °C range, shown in the DSC curve in Fig. 1(b), indicates a non-oxidative decomposition of carbonate residues, which is correlated to the mass loss observed in the TG curve at the same temperature range. The E600 sample

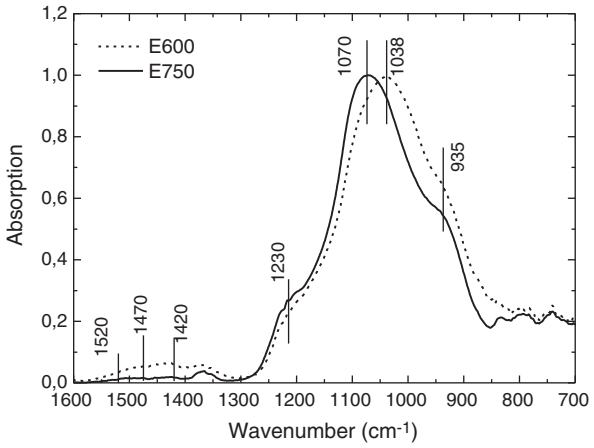

Fig. 2. FT-IR spectra of the E600 and E750 samples.

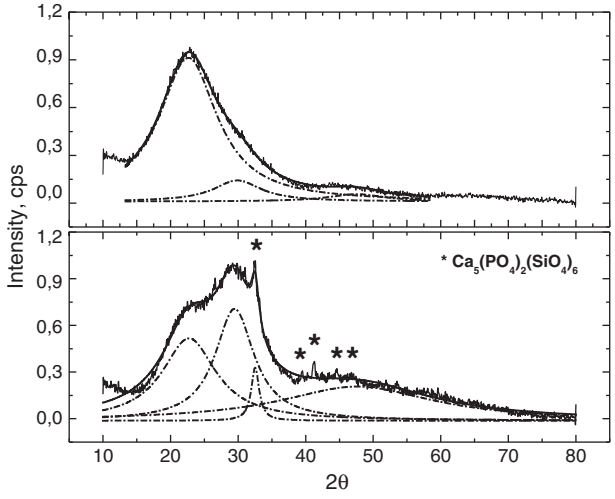

Fig. 3. X-ray diffraction patterns of BG samples annealed at 600 and 750 °C.

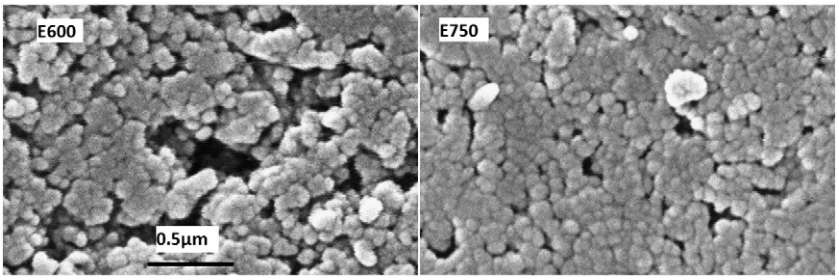

Fig. 4. 50K magnification SEM micrographs of the E600 and E750 samples.

exhibited a glass transition temperature (T_g) around 820 °C as well as peak temperatures of first (T_{c1}) and second (T_{c2}) crystallizations at 890 and 1020 °C respectively.

Although the temperature of 600 °C has been used in several studies to stabilize the sol–gel samples, here the BG samples synthesized by sol–gel emulsion were also annealed at 750 °C for 2 h. This annealing temperature was chosen taking into consideration that the release of impurities from the samples is almost complete at this temperature. Furthermore, it is lower than T_g and T_{c1} of the BG samples, thus this annealing should prevent cluster formation, sintering and thermally-activated crystallization of the samples.

3.2. FT-IR measurements

Fig. 2 shows the mid-infrared spectra of the BG samples stabilized at 600 and 750 °C. The bands centered at 1420, 1470, and 1520 cm^{-1} in the E600 sample can be assigned to asymmetric stretching of $(CO_3)^{2-}$ groups, which are residual carbonates inherent to the sol–gel reaction [8]. In contrast, the E750 sample did not exhibit these bands, since the carbonates were removed during the stabilization procedure.

All infrared spectra displayed a broad band spanning between 850 and 1300 cm^{-1}, which was composed of bands located at about 1230, 1070 and 1038 cm^{-1} assigned to the Si–O–Si stretching mode; and a band centered at 935 cm^{-1} corresponding to the vibrational mode of stretching of Si–O–NBO [8]. Absorption bands in the 900–970 and 1000–1100 cm^{-1} range have also been associated with stretching vibrations of PO_4^{3-} groups, so that, despite the low concentration of phosphates in the glass matrix, their role is not ruled out [8].

3.3. X-ray diffraction and microstructure measurements

Fig. 3 shows the XRD patterns of the E600 and E750 samples. The XRD pattern of the E600 sample shows two broad halos centered at about 22° and 31°, indicating not only that crystallization did not occur, but also the existence of two amorphous phases. The halos observed in the XRD pattern of the E600 sample are also observed in the pattern of the E750 particles. However, the halo at about 31° in the E750 sample, which appeared as a shoulder in the pattern of the E600 sample, is predominant over the halo located at around 22°. Therefore, the annealing temperature plays an important role in the determination of the relative amount of the amorphous phases in the samples synthesized by the emulsion method. Moreover, the sample annealed at 750 °C showed an incipient crystallization of the $Ca_5(PO_4)_2(SiO_4)_6$ phase (JCPDS 83-1494).

The micrographs of the E600 and E750 samples shown in Fig. 4 reveal primary particles with diameters less than 100 nm, which are agglomerated. The results also indicate that the sample annealed at 750 °C did not undergo sintering, preserving the same microstructural characteristics of the E600 sample.

3.4. Bioactivity

Fig. 5 displays the SEM micrographs of the E600 and E750 pellet samples as prepared and after 4 and 7 days immersed in simulated body fluid (SBF). The micrographs reveal the formation of spheres over the entire surface of the pellets, as a result of the interaction between glass particles and the SBF. Enlarged images of the surfaces show that spheres with similar diameters were formed (Fig. 6).

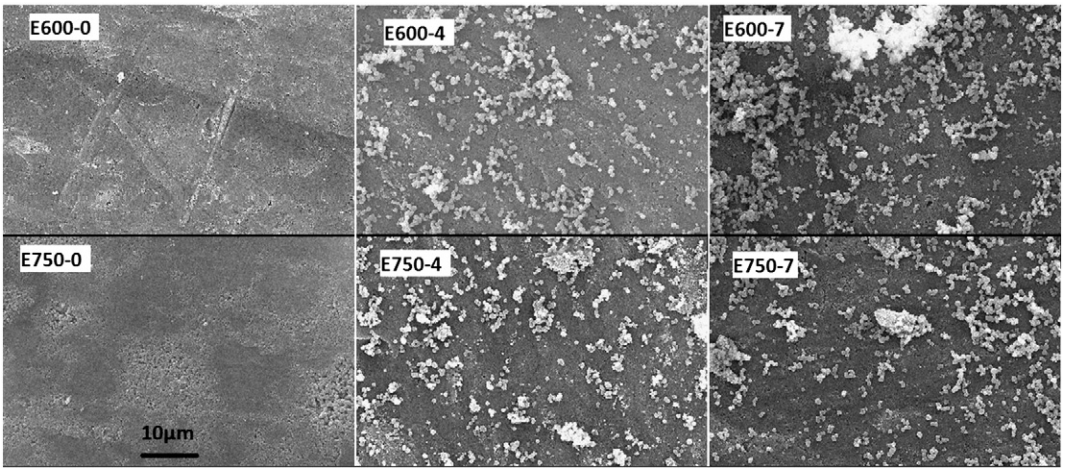

Fig. 5. 2K magnification SEM micrographs of the E600 and E750 samples.

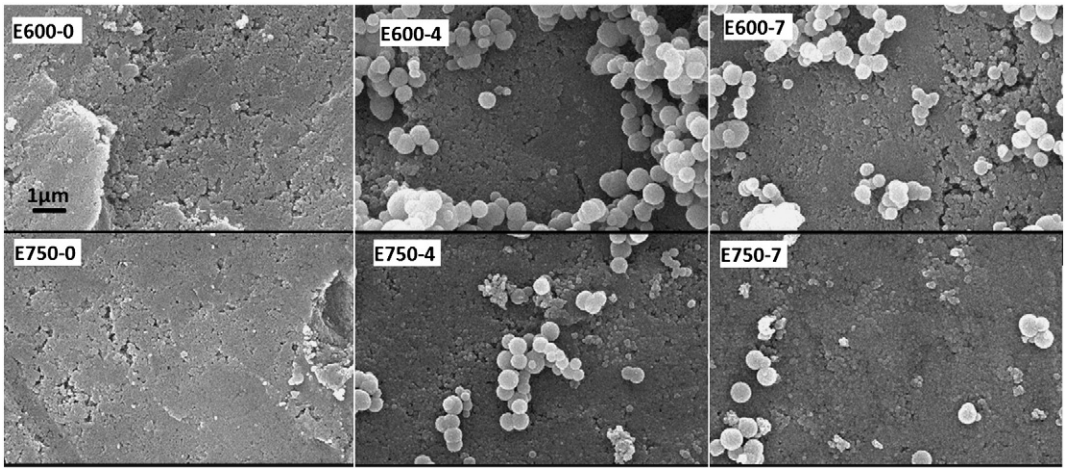

Fig. 6. 10K magnification SEM micrographs of the E600 and E750 samples.

EDS measurements were performed to evaluate the relative concentrations of Ca and P present on the surfaces and spheres resulting from the immersion time in SBF. The Ca/P ratios on the surfaces of the E600 and E750 samples after 4 days of soaking were about 3.7 and 2.6, respectively. After 7 days of immersion, Ca/P ratios of approximately 3.3 and 2.2 were obtained for the E600 and E750 samples, respectively. On the other hand, the spheres formed on the E600 and E750 pellets that were soaked for 4 days exhibited Ca/P ratios of about 2.0 and 1.6, respectively, while the spheres observed on the samples soaked in SBF for 7 days showed ratios of 1.6 and 1.4 for the E600 and E750 samples, respectively. The ratios observed for the spheres are similar to that expected for the stoichiometry of hydroxyapatite (~1.7), indicating the bioactive response of the samples.

The mid-infrared spectra of the samples in the 800–1300 nm range prior to and following SBF immersion, shown in Fig. 7, also corroborate the bioactivity of the samples, due to the decrease of the Si–NBO band located at around 935 cm^{-1}. Several studies have shown that the formation of hydroxyapatite is followed by the reduction of this band [15–17].

4. Conclusions

The findings of this study indicated that the sol–gel emulsion method is appropriate to produce bioactive glasses without crystallization and carbonate residue. In addition, the SEM micrographs indicated that emulsion is a promising approach to synthesize particles with diameters below 100 nm. The BG samples thermally stabilized at 600 and 750 °C exhibited different glassy structures, indicating that it is possible to manipulate the amorphous feature of the samples.

Acknowledgments

Financial support from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FUNDECT (Fundação de Apoio ao Desenvolvimento do Ensino, Ciência e Tecnologia do Estado de Mato

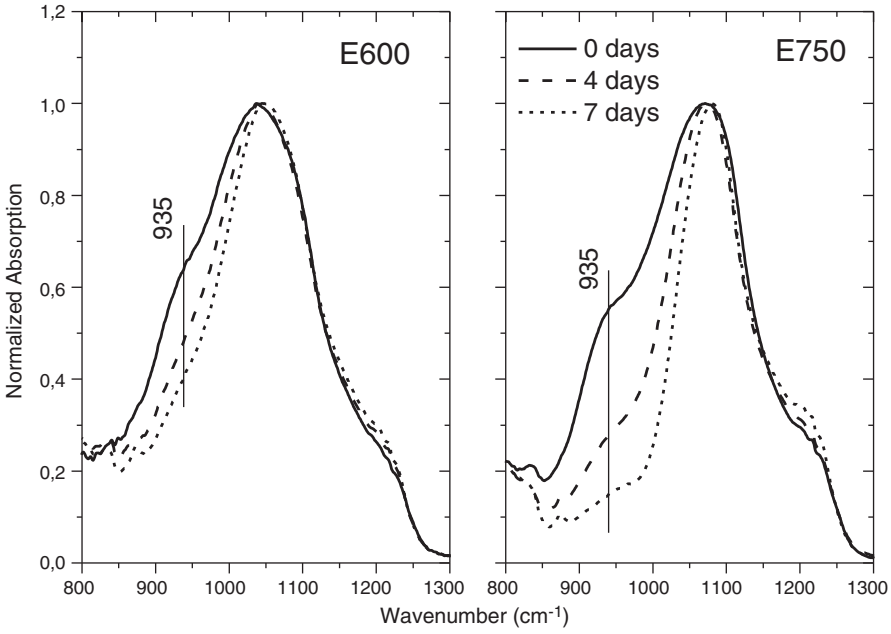

Fig. 7. FT-IR spectra of the E600 and E750 samples as prepared and following 4 and 7 days of immersion in simulated body fluid.

Grosso do Sul) is gratefully acknowledged. This study was performed under the auspices of the "INCTMN/CNPq" and "National Institute of Photonics/CNPq".

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