Applied Surface Science 255 (2008) 391–395

Contents lists available at ScienceDirect

Applied Surface Science

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

Effects of Mg and Zn on the surface of doped melt-derived glass for biomaterials applications

E. Dietrich, H. Oudadesse *, A. Lucas-Girot, Y. Le Gal, S. Jeanne, G. Cathelineau

Université de Rennes1, SCR, UMR CNRS 6226, 263 av du Général Leclerc, 35042 Rennes, France

ARTICLE INFO

Article history:
Available online 26 June 2008

PACS:
81.05.Mh
82.65.+r
87.64.Je

Keywords:
Glass
In vitro
In vivo
Bone
Graft
Interface(s)
Surface

ABSTRACT

Bioactive glasses in the system SiO_2–CaO–Na_2O–P_2O_5 were synthesized pure and doped with magnesium or zinc by melt-derived method. The bioactivity was studied during *in vitro* assays: the ability of hydroxycarbonate apatite (HCA) layer to form on the glass surface was examined after contact with simulated body fluid (SBF). The X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) studies were performed before and after immersion *in vitro* assays. The SBF solutions were also analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Introduction of magnesium and zinc as trace element induces several modifications on the observed phenomena at the glass surface and in SBF solution after immersion of the samples. The chemical durability of the glasses, the formation of the silica-rich layer and the crystallization of the HCA layer were affected, but not present the same modifications as the introduced doping element.

1. Introduction

Certain compositions of glasses in the system SiO_2–CaO–Na_2O–P_2O_5, used as biomaterials, are able to form a bond with bone once they are implanted, such as the Bioglass® [1,2]. In fact, when this glass is immersed in biological fluids, a layer of hydroxyapatite (HA) similar to the mineral phase of bones is formed on its surface. A controlled surface reaction of the bioactive glass is an important factor governing its bioactivity and it depends on many factors. By varying the chemical nature and concentration of elements, new important physico-chemical and biological properties can also be added and the glass can be tailored to specific orthopaedic or dental applications.

Magnesium and zinc are two elements that present high physiological interests in the biomedical field. Mg is essential to human metabolism and is naturally present in bony tissues [3,4]. It may actually have stimulatory effects on the growth of new bony tissues [5,6] and it is classified as an essential minor element [7]. Zn is also an essential trace element which presents effects on *in vitro* and *in vivo* bone formation [8,9]. It promotes the proliferation of osteoblasts [10] and many biological functions. It advantages the bone formation around the implant and accelerates recovery of the patient [11]. The aim of this study is focused on surfaces behaviour of pure and doped with magnesium and zinc 46S6 glasses to evaluate their bioactivity and to compare the effects of the doping elements on the HCA formation. In this work, we report the synthesis and the surface behaviour using the *in vitro* studies of melt-derived glasses based on 46S6 composition (46 wt% SiO_2, 24 wt% CaO, 24 wt% Na_2O and 6 wt% P_2O_5) with introduction of Mg or Zn as doping element.

2. Materials and methods

2.1. Glass elaboration and in vitro assays in SBF

The composition of the glass 46S6 is based on a modification of the Bioglass® composition and is used as reference to validate our experimental procedure. This composition is also studied doped by introduction of Mg between 0.4 and 1.2 wt% (46S6Mg*X*, $4 \leq X \leq 12$) or Zn between 0.02 and 0.1 wt% (46S6Zn*Y*, $2 \leq Y \leq 10$). These elements were introduced according to their amounts stored in bony tissues, respectively, about 5 mg/g and 177 μg/g.

For elaboration, calcium metasilicate, sodium metasilicate, sodium metaphosphate and magnesium/zinc oxide are weighed and mixed in a polyethylene bottle for 45 min using a planetary

* Corresponding author.
E-mail address: hassane.oudadesse@univ-rennes1.fr (H. Oudadesse).

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doi:10.1016/j.apsusc.2008.06.094

mixer. Premixed batched were melted in Pt crucible at 1300 °C for 3 h. Samples were cast in preheated brass molds, to form cylinders of 13 mm in diameter and 10 mm in height, and annealed for 4 h at the glass transition temperature of each composition: respectively 522 °C for 46S6Mg12 and 536 °C for 46S6Zn10. The thermal properties of these glasses (glass transition, crystallization and fusion temperatures) were studied by differential thermal analysis from room temperature to 1400 °C.

To evaluate the bioactivity, the samples were soaked in 8 mL of a SBF solution at 37 °C and pH 7.4. Only one face of the glasses was in contact with SBF and the liquid/glass surface contact ratio was of about 1.33 cm^2. SBF solution mimics the inorganic composition of human body fluids and was prepared according to the Kokubo's procedure [12]. After the various immersion periods, the samples were removed from the fluid, washed and dried at room temperature. Their surfaces and morphology of particles surface were studied using XRD and SEM methods. The newly formed layer was detached by scarping the glass surface and bulk group vibrations were analyzed by FTIR technique.

3. Results and discussion

The amorphous character of glasses before immersion in the SBF was confirmed by XRD analyses (Fig. 1). The IR spectrum of glasses before immersion (Fig. 4) presents several broad absorption bands. The complex band in the region 1200–900 cm^{-1} includes absorption due to both PO and SiO_2 groups. The bands at 1000 cm^{-1} correspond to the vibrational mode of asymmetric stretch of Si–O and the strong band at 506 cm^{-1} corresponds to the vibrational mode of the bending Si–O–Si. The SEM observation (Fig. 5) showed that the surfaces of samples are smooth and non

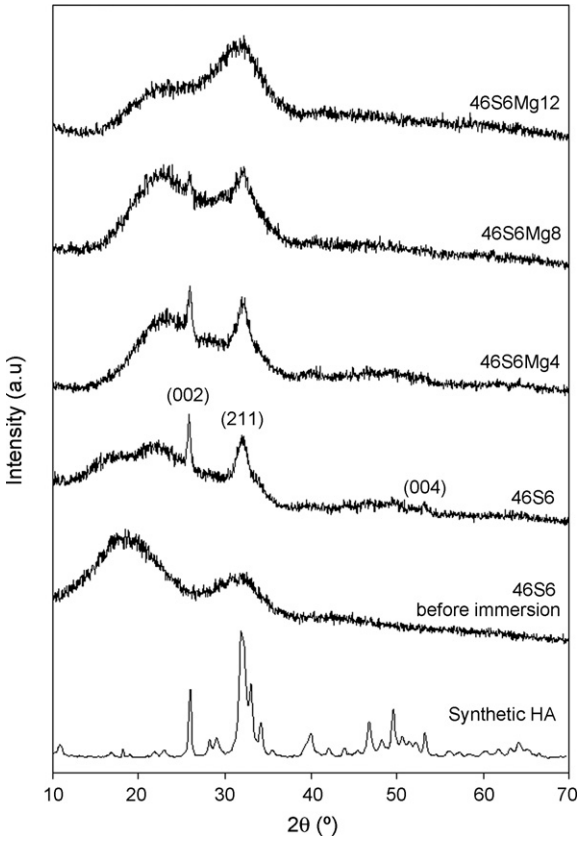

Fig. 1. XRD patterns of 46S6 and doped glasses 46S6Mg*X* ($4 \leq X \leq 12$) after a 30-day *in vitro* assay in SBF.

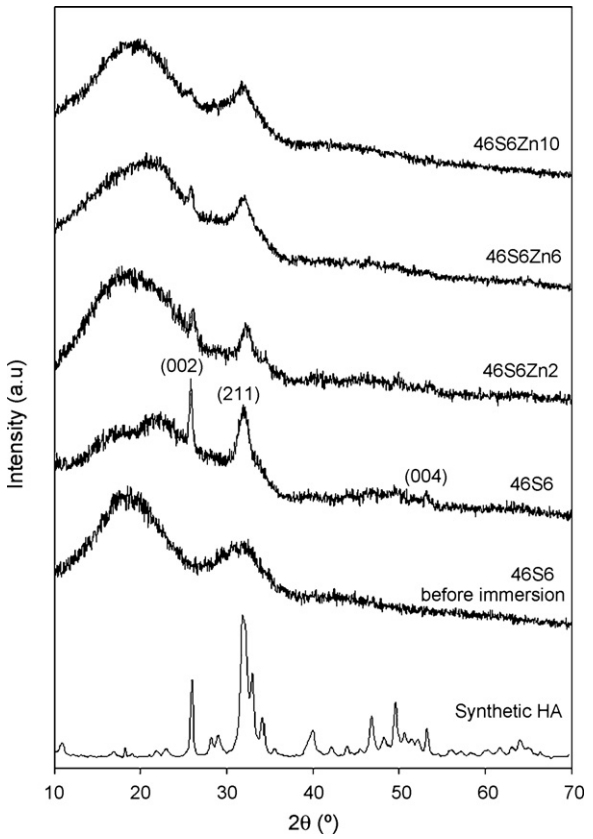

Fig. 2. XRD patterns of 46S6 and doped glasses 46S6Zn*Y* ($2 \leq Y \leq 10$) after a 30-day *in vitro* assay in SBF.

porous before *in vitro* assays. After soaking in SBF, modifications of the glasses surfaces and SBF composition were registered.

The XRD patterns for doped glasses 46S6Mg*X* ($4 \leq X \leq 12$) and 46S6Zn*Y* ($2 \leq Y \leq 10$) after a 30-day *in vitro* assay in SBF are presented on Figs. 1 and 2. The diagram of pure hydroxyapatite is used as reference. The formation of apatite in SBF is confirmed with three diffraction maxima at 26°, 32° and 53° (2θ) that correspond, to the (0 0 2), (2 1 1) and (0 0 4) apatite reflections [13]. Concerning Mg-doped glasses, the (0 0 2) apatite reflection decreases in intensity until it disappears and the (2 1 1) reflection becomes broader when the Mg content increases. For Zn-doped glasses, the same modifications are observed than for Mg-doped glasses and (0 0 4) reflection disappears when the Zn content increases.

The FTIR spectra of the compounds scrapped on the glass surfaces after immersion are presented in Figs. 3 and 4. They have been normalized to the more intense band at around 1080 cm^{-1}. For all compositions, the precipitation of the calcium phosphate layer is confirmed by the presence of three well-defined phosphate bands at 565, 603 and 961 cm^{-1}, characteristic of phosphate in crystalline phases. Moreover, the presence of carbonate bands at 873, 1420 and 1470 cm^{-1} indicates the formation of a hydroxycarbonate apatite (HCA) [14]. Careful inspection of the spectra for various Zn contents reveals variations of the positions or intensities of the reflection bands on Fig. 4. The following changes were observed after 30 days of immersion with the increase of Zn content: the intensity of the band 470 cm^{-1} (Si–O–Si bend) became very low, the band at 795 cm^{-1} (Si–O–Si symmetric stretch) and the shoulder at 1220 cm^{-1} (P═O stretch) decreased in intensity until to disappear for 46S6Zn8 and 46S6Zn10 and the band at 1080 cm^{-1} was shifted to 1040 cm^{-1} (Si–O–Si asymmetric stretch). On Fig. 3, for Mg-doped glasses, among the bands already