

A crystalline layer is apparent on the surface of both glasses and EDS analysis confirms the presence of Ca and P with Ca:P ratios of (a) 1.64 (GN2) and (b) 1.72 (GFN2). These values compare well with the theoretical value of 1.67 for hydroxyapatite.

The results show that the bioactivity of the glasses is highlighted by the nucleation of a HCA layer and that this bioactivity decreases slightly with the increase of the nitrogen rate. In vitro studies in SBF have been completed by cytotoxicity tests. They showed the noncytotoxicity of oxynitrides and of oxyfluoronitrides glasses regardless of the nitrogen ratio introduced. Finally, a bacteriological study showed that there is practically no formation of biofilms on the surface of G2FN0 and G2FN4 bioactive glasses.

### 3.5 SOL-GEL QUATERNARY BIOACTIVE GLASSES AND THEIR SILVER DOPING

#### 3.5.1 Overview

The sol-gel method consists mainly of replacing the vitreous network-forming oxides traditionally melted at high temperature by homologous soluble and polymerizable precursors in organic media. Silicon alkoxide (tetraethylorthosilicate, TEOS) and phosphorus alkoxide (triethylphosphate, TEP) are used. They have the ability to hydrolyze and to condense quite easily in the presence of water (Lázaro et al., 2014; Elisa et al., 2010). Modifiers, such as calcium and sodium, could be added to the two precursors, forming a sol. The hydrolysis reactions are initiated by the addition of water and a catalyst. Then, the gel (Audebert and Miomandre, 2005) is formed in the solvent by condensation reactions between the hydrolyzed groups of the formers. This reaction is called gelling and the time required for gel formation is called gel time. Gelation occurs when macromolecules are formed and touch each other, giving a solid appearance to the gel. The condensation reactions continue after the gel has formed, leading to a progressive aging called syneresis.

During the syneresis of the gel, the condensation reactions lead to a macroscopic contraction of the gel and to a shrinkage of its porosities. This has a negative impact on the mechanical strength of the samples, which will become fragile and subject to cracking (Audebert and Miomandre, 2005). It is one challenge of sol-gel synthesis: it is difficult to obtain massive samples without using drying under supercritical conditions. It is for this reason that the development of a sol-gel technique that allows the production of bioactive glass deposits has been chosen.

Once the syneresis has been completed, the gel must be dried (Balamurugan et al., 2008). The water and the organic solvents are thus evaporated. To carry out this operation quickly, the gel is placed in an oven at 130°C. When a Differential Thermodynamic Analysis (DTA) is carried out on a dry sample, a stabilization of the amorphous lattice is observable through a decrease in the