Raman spectroscopic and bioactivity studies on silicate glasses

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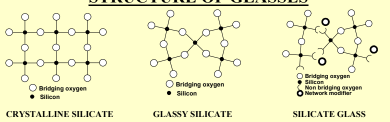
INTRODUCTION

AIM

- Quantification of non-bridging silicon-oxygen groups (Si-O-NBO) in SiO_2 based glasses by Fourier Transform Raman Spectroscopy.
- Study of the *"in vitro"* bioactivity dependence of the glasses on the Si-O-NBO concentration.

STRUCTURE OF GLASSES



* Open amorphous structure.

* Breakage of some of the Si-O-Si bonds.

* Introduction of network modifiers : Na^+, K^+, Ca^{2+}.

* Formation of non-bridging silicon-oxygen bonds (Si-O-NBO).

PROCEDURE

BEFORE IMMERSION IN SIMULATED BODY FLUID:

- Structural study of bioactive glasses by Fourier Transform Raman Spectroscopy (FT-Raman).

AFTER IMMERSION IN SIMULATED BODY FLUID:

- Surface morphology study by Scanning Electron Microscopy (SEM).
- Bioactivity study (identification of calcium phosphate and silica-rich layers) by Energy Dispersive X-ray Spectroscopy (EDX).

EXPERIMENTAL

BIOACTIVE GLASSES

Glass	SiO_2	Na_2O	CaO	P_2O_5	B_2O_3
BG45	45	24.5	24.5	6	-
BG53	53	23	20	4	-
BG59	59.7	25.5	11	2.5	1.3

Composition in % wt

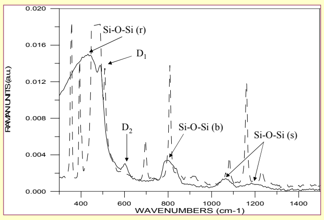
IN VITRO TEST

- Simulated Body Fluid (SBF K9).
- Volume of SBF: 50 ml.
- Incubator temperature: 36,5 ºC.
- Immersion time: 72 hours.

RESULTS

A) STRUCTURAL STUDY BY FT-RAMAN BEFORE IMMERSION IN SBF

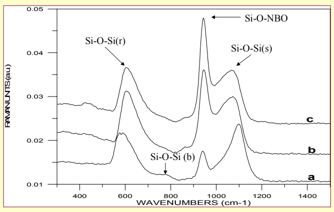
RAMAN SPECTRA OF REFERENCE MATERIALS



Fused silica (v-SiO_2) : Solid line.
Quartz (c-SiO_2) : Dashed line.

- 453-490 cm^{-1} ⇒ The oxygen atom moves perpendicular to the Si-O-Si plane. (Rocking vibration)
- 783-837 cm^{-1} ⇒ The oxygen move at right angles to the Si-Si lines, in the Si-O-Si plane.(Bending vibration).
- 1064-1183 cm^{-1} ⇒ The bridging oxygen atom moves parallel to the Si-Si lines in the oposite direction to their Si neighbours.(Stretching vibration).
- D_1 and D_2 ⇒ Defect lines ⇒ Rings of bonds in the glass structure.

RAMAN SPECTRA OF BIOACTIVE GLASSES

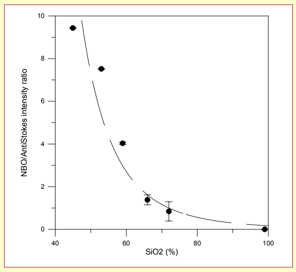


a) BG59, b) BG53, c) BG45

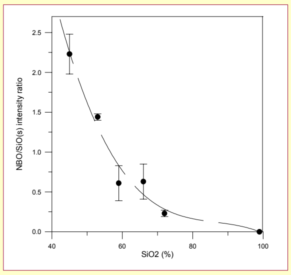
- For decreasing silica content, an additional absorption band at 900-950 cm^{-1} emerges, being associated to the non-bridging-oxygen bond (Si-O-NBO).
- When the alkali and alkali-earth ion content in the glass decreases, the peaks corresponding to stretching and rocking vibrations shift to larger and shorter wave- numbers, respectively.
- The intensity of all Raman lines increases with the incorporation of alkali and alkali-earth elements in the SiO_2 matrix.

CORRELATION PLOTS

- The appearance of the anti-Stokes line at 860 cm^{-1} for glasses of different composition has been observed.
- This Raman spectral feature was not found for fused silica glass or quartz.



Intensity ratio of the Si-O-NBO band and the anti-Stokes line at 860 cm^{-1} for glasses of different compositions.

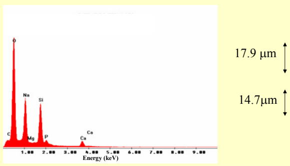


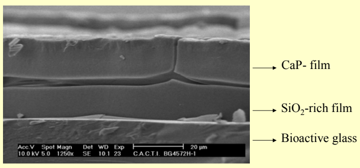
Ratio of intensities of the Si-O-NBO band and the Si-O-Si stretching vibration as a fuction of the silica content

- An increase of the alkali and alkali-earth elements in the silica network leads to a higher concentration of Si-O-NBO bonds.
- This plot allows to quantify the Si-O-NBO concentration using a non-destructive tool such as Raman spectroscopy.

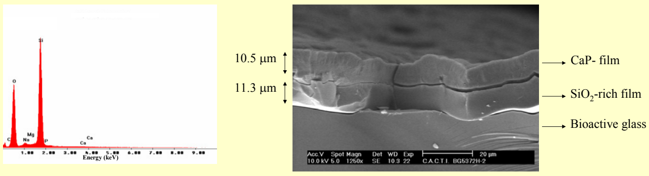
B) BIOACTIVITY STUDIES AFTER IMMERSION IN SBF

BIOACTIVITY STUDY

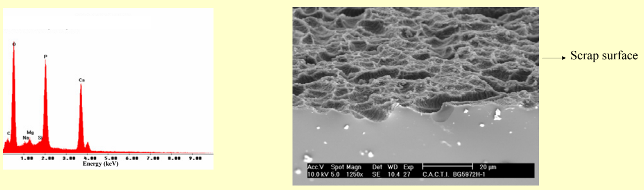




BG 45



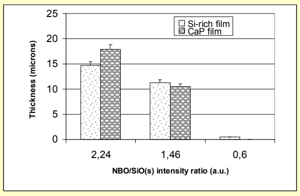
BG 53



BG 59

Cross-section analysis by EDX and SEM of three different glasses

- The thickness of the calcium phosphate and the silica-rich layers increases when the silica content in the glass decreases.
- An increase of the number of structural units including Si-O-NBO groups facilitates the ionic exchange with the SBF leading to the formation of a thicker calcium phosphate film.



Thickness of calcium phosphate and silica-rich layers after immersion of bioactive glasses in SBF for 72 hours.

CONCLUSIONS

- Raman Spectroscopy is a powerful technique for the analysis of bioactive glasses:
  - Identification of Si-O-NBO groups.
  - Changes in the Si-O-NBO bond environment.
- A minimun concentration of Si-O-NBO groups (NBO\SiO(s)>1) is required in order to have an efficient bioactive process.