

The glasses are then noted with P, followed by the value of  $x$ , to which their original name in the ternary is added. For example C1 glass, into which 1%  $P_2O_5$  has been introduced, has been denoted P1C1. It belongs to the  $PxC1$  series (glass C1 +  $x\%$  of phosphorus).

In order to limit the number of glasses studied, a selection of glasses, one for each bioactivity domain of the ternary  $SiO_2$ -CaO- $Na_2O$ , was made.

The maximum amounts of  $P_2O_5$ , which can be introduced into the compositions of the ternary system, are limited to 6 mol%. Indeed, above this value and even below it in certain cases, the compounds are no longer vitreous.

Different ratios of phosphorus have been introduced for the same basic composition of ternary glasses in order to observe the influence of this phosphorus content on bioactivity. The glasses are obtained by melting them at high temperature and quenching.

For the domain of greatest bioactivity (12 and 22 h), C2 was selected. For the medium bioactivity range (2 days), B5 was chosen. Finally, to cover the whole area of less efficient bioactivity (3–4 days), the compositions selected were A1, A3, and B3.

As an example, the formulations of the  $PxC2$  glasses are:

P1C2: 44.55%  $SiO_2$ -23.265% CaO-31.185%  $Na_2O$ -1%  $P_2O_5$ .

P3C2: 43.65%  $SiO_2$ -22.795% CaO-30.555%  $Na_2O$ -3%  $P_2O_5$ .

P5C2: 42.75%  $SiO_2$ -22.325% CaO-29.925%  $Na_2O$ -5%  $P_2O_5$ .

### 3.2.3 Bioactivity of $SiO_2$ -CaO- $Na_2O$ - $P_2O_5$ System

#### 3.2.3.1 Bioactivity in Terms of Time of HCA Layer's Nucleation

As for the glasses of the ternary  $SiO_2$ -CaO- $Na_2O$ , the surfaces of the P-doped glasses are analyzed by FTIR spectroscopy, before and after soaking in SBF. The different stages have made it possible to identify the groups present in the glasses and to understand the bioactivity mechanisms and the reactivity.

Grussaute (1998) noted that the introduction of phosphorus into the vitreous networks has two effects on the structure:

- the addition of phosphorus leads to the formation of phosphate-modifier complexes. These new entities have low binding forces compared to those of the initial glass,
- there is also a repolymerization of the silicate network because the negative charges of the orthophosphate units ( $PO_4^{3-}$ ) are compensated by cations taken from the network-modifying ions. The network is then strengthened.

Moreover, according to recent  $^{29}Si$  and  $^{31}P$  NMR studies applied to calcium silicate glass with 2.6 mol% of  $P_2O_5$ , the glass structure exhibits phosphate clusters of 5 and 6  $PO_4$  tetrahedral units embedded in the silicate network and a few percentage of  $PO_4$  acts as end-chain units of the silicate network (Faron et al., 2013).

The glasses, which are inverted glasses, remain so and their structures present a predominant number of nonbridging oxygens (NBOs).