Bioactive glasses and biocompatible ceramic materials based on P_2O_5

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Ph.D. Thesis

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ABSTRACT:

In the present ph.D. Thesis, it is reported the synthesis of binary phosphate glasses with magnesium $xMgO\cdot(1-x)P_2O_5$, where $0.50\leq x\leq 0.80$ and calcium $xCaO\cdot(1-x)P_2O_5$, where $0.50\leq x\leq 0.72$. The synthesis of glasses with such a high content of alkali is reported for the first time in the literature and was achieved by fast quenching of high temperature melts (10^5 °C/s) using a twin-roller device. Every glass structure was studied by Raman and IR spectroscopy and the results have shown that the glassy network consists of phosphorous tetrahedra that are connected with each other creating long chains, can be modified with the addition of the magnesium and calcium oxides. The addition of the oxides induce the disruption of the P-O-P bridges that connect the phosphate tetrahedra into chains and the glassy network turns out to consists almost exclusively of isolated tetrahedral.

The Raman and IR spectra have shown that the calcium cations act more as modifiers than the magnesium cations which seems to create bridges with the oxygens configuring Mg-O unit clusters. The nature of the cations and the reactions between them was able to be theoretically studied by molecular dynamics simulations which result to the same conclusion as above.

The induced nucleation and crystallization after two step heat treatment of the calcium phosphate glasses of x=0.67, 0.70 and 0.72 lead to glassceramics that reveal crystalline phases with bioactive properties such as β-TCP and α, β-DCP according to X-rays diffraction results.

By the fast quenching of high temperature melts method, it was able to be synthesized ternary phosphate glasses $xB_2O_3 \cdot [yCaO \cdot (1-x)P_2O_5]$, where x=0, 0.1, 0.2, 0.3 και y=2, 2.6, 3, 4, 5. The structure of these glasses was studied by Raman and IR spectroscopies. The analysis of the spectra for the majority of the samples has shown that the glassy network consists mostly of phosphate units with high negative charge such as $P_2O_7^{4-}$, PO_4^{3-} and triangular borate units such as $B\varnothing_2O^-$. In ternary glasses, the modification of the phosphate lattice by the calcium oxide seems to be dawdled as a number of the Ca^{2+} cations can also act as modifiers of the boron lattice that generates at the same time with the phosphate lattice. During in vitro experiments, the glasses with boron immersed into simulated body fluid (SBF) for a few days and the Raman and IR spectra revealed that all the samples have shown bioactivity.

In order to understand the mechanism in which hydroxyapatite forms on the surface of a representable $0.64CaO\text{-}0.16P_2O_5\text{-}0.20B_2O_3$ ternary glass, the glass remained into SBF for variety durations and afterwards surveyed by Raman and IR spectroscopies that submitted hydroxyapatite forming on the glass surface even after a few hours immersion in the body fluid. Observations by optical and electronic microscopy have shown that there are changes that occur on the glass surface that can be attributed to the development of microcrystalline apatite over the glassy surface.

Through atomic absorption measurements in the SBF fluids it was possible to calculate the concentrations of Na^+, Ca^{2+} and $B(OH)_4^-$ ions where the results have shown that Ca^{2+} cations abandon step-by-step the surface of the glass as result of the ionic exchange that take place in the middle surface between glass and fluid during the first hours of the immersion. In the same rate $B(OH)_4^-$ ions abandon the glassy surface because of the corrosion of the glassy network. The chemical analysis EDX, on the surface microcrystallines confirmed the forming of boroapatite with fluctuant boron percentage up to 10mol%. Joint with the pH measurements in the same SBF fluids and the Raman and IR spectra, it was ascertained maximum apatite's formation during the first stages whereas its crystalline structure alters by time from boroapatite to hydroxyapatite. Effective role in the bioactivity of the glasses seems to play the formation of $P\text{-}OH^-$ and $B\text{-}OH^-$ groups on the glasses surfaces.

The biocompatibility and the non-toxicity of two $0.72CaO\text{-}0.18P_2O_5\text{-}0.10B_2O_3$ and $0.64CaO\text{-}0.16P_2O_5\text{-}0.20B_2O_3$ representable glasses was examined by incubation of osteoblasts from rat calvariae primary culture in a solution with concentration

0,005gr bioglass powder/ml RPMI medium. The research was focused to the cell's viability and proliferation and to alkaline phosphatase and collagen production. Generally, both glasses behaved normally and, in a matter of a first researching level, the coexistence between glasses and biological cells doesn't run any risk.