Synthesis and characterization of the bioactive ternary SiO2-CaO-P2O5 Bioglass

Aymen Hadji, Abdelali Merah, Ouanassa Guellati, Mohamed Guerioune

Abstract— **In this paper, we present our results on the synthesis and characterization of silicon dioxide or silica calcium oxide and phosphorus pentoxide (SiO2-CaO-P2O5) glass; by means of the sol-gel method where previous works have used tetraethyl orthosilicate (TEOS) as SiO2 precursor, but here we are using the commercialized aerosol SiO2. Indeed, our synthesis of this gel-glass nanocomposite was carried out using the aerosol SiO2, calcium nitrate tetrahydrate (CaNO3.4H2O) and sodium hydrogenphosphate (Na2HPO4) as precursors of SiO2, CaO and P2O5 respectively. The characterization was carried out by infrared spectroscopy (FTIR), X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM) to study their chemical bonding, structural and morphological properties of the resulting amorphous glass. These techniques conducted us to detect the chemical modifications induced by modifying the Ca/P molar ratio. In addition, the thermal properties of the synthesized gel-glass materials were studied using thermogravimetric and differential thermal analysis (TG/DTA). The results revealed that the glass transition temperature is around 600°C, with the aim to convert them into ceramic powders through calcinations treatment. The results gave us porous bioactive materials that can be suitable for many applications such as prolonged-release drug or bone tissue repairing.**

Index Terms— **Bioglass, Sol-Gel, Synthesis, Structural and Morphological Characterization.**

I. INTRODUCTION

The first bioglass (45S5) was discovered in 1971 by Hench at al. [1]. Its composition was 46.1 mol% SiO_2, 26.9 mol% CaO, 24.4 mol%Na_2O and 2.5 mol% $P2O_5$. Since then, many researchers explored many compositions, using different kind of oxide and varying the percentage of added molar in the considered composition, taking into account the preparation method used. It is proved in that the glasses or ceramics obtained by the sol-gel method are more bioactive than the ones via other methods such as merging [2, 3 and 4]. Among the advantages of this method, it is known by the fact of ensuring good homogenisation of reactants and uniformity of the obtained gel, preventing phase separation.

In the work of Michelina Catauro et al (2015) [4], the authors have studied the ternary SiO_2-CaO-P_2O_5 systems using tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) precursor, where the particularity of this ternary systems is the bioactivity leading to many applications. However, our work studied the same systems using aerosol SiO_2 commercial precursor, by adapting the sol-gel method.The development of bioactive glasses is a part of a multidisciplinary approach. This family of substitutes is particularly adapted to:

1- Active ingredients of sustained-release drugs, the developments of bioactive system have shown that the drug relay from the publication of the synthesized porous bio-glasses is controlled by a diffusion mechanism.

2- The filling of bone defects, where in contact with living tissue, bioactive glasses produce a series of physic-chemical reactions at the material/bone tissue interface that lead to the formation of a calcium phosphate layer. The evolution of this layer gives it a structure similar to that of the mineral phase of the bone, which allows an intimate bond between the bioactive glass and the host tissues. It is this bond which characterizes the bioactivity of the material.

So, our aim in this paper is based on the research of how to develop the SiO_2-CaO-P_2O_5 bioglass composites, and processing them, using simple and low cost sol-gel method, with the goal of extracting interesting and promising properties for some applications.

II. METHODS AND MATERIALS

In this section we present material, precursors and techniques to synthesise the ternary SiO_2-CaO-P_2O_5 bioglass .

A. *Synthesis process*

Our bioglass was synthesized using the sol-gel procedure starting from aerosil (SiO_2, Melun French pharmaceutical cooperation powder 99,8%), calcium nitratetetrahydrate ($Ca(NO_3)_2$•$4H_2O$, Sigma Aldrich 99.997%, crystals and lumps) and disodium hydrogen phosphate anhydrous (Na_2HPO_4,GPR RECTAPURgranulated 99%) precursors of SiO2, CaO and P_2O_5, respectively.

This was done in the following way: (see diagram Figure 1)

Step 1:

- First we add the aerosil to deionised water and put it in a magnetic stirrer.
- Keep adding NaOH to the obtained substance until the obtention of pH=10.
- After 30 min of stirring, we add calcium nitratetetrahydrate.
- Stir for 30 min again, and then add disodium hydrogen phosphate anhydrous.

At this step we obtain a homogenous substance, namely “gel” (see image 1)

Aymen Hadji, Laboratory of Pharmaceutical Mineral Chemistry & Mathematical Modeling and Numerical Simulation Research Laboratory, Badji-Mokhtar University, Annaba, Zaafrania P.O. Box 205, 23000, ALGERIA, Mobile No: +213664818906

Abdelali Merah, Laboratory of Pharmaceutical Mineral Chemistry, Faculty of Medicine, Badji-Mokhtar University, Annaba, Zaafrania P.O. Box 205, 23000, ALGERIA

Ouanassa Guellati, LEREC Laboratory, Department of Physics, Badji-Mokhtar University, Annaba, P.O. Box 12, Annaba 23000, ALGERIA

Mohamed Guerioune, LEREC Laboratory, Department of Physics, Badji-Mokhtar University, Annaba, P.O. Box 12, 23000, ALGERIA

Step 2:

• We leave the gel for 24h at ambient temperature to get mature.

• We proceed to filtration and cleaning the gel by deionised water until the obtention of pH=7.

• We dry it at 80°C during 24h in an oven, and then we ground the product in an agate mortar, to get a fine white powder (see image 2).

A. Characterization techniques

The synthesized materials were extensively characterized in order to mainly study the effect of experimental parameters on the structure, morphology and elemental composition. The structural characterization of our products were investigated by powder X-ray diffraction (XRD) using an XRD D8 ADVANCE-BRUKER (EQUINOX 3000 INEL) diffractometer equipped with a copper anticathode tube "Cu Kα radiation" (λ = 1.5406 Å) and a graphite monochromator rear blade, operating at 40 kV and 40 mA with a scanning rate of 0.2 °.s^{-1}. The XRD patterns of all specimens were recorded in the [10° - 90°] 2θ range.

Fourier-Transform Infra-red (FTIR) spectra of these products were recorded using a Bruker Vertex 77v spectrometer in the

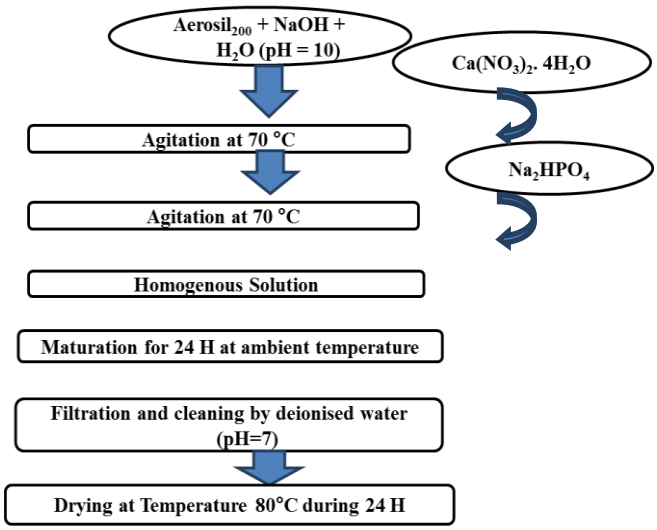

Figure 1: Diagram of operating mode for SiO_2-CaO-P_2O_5 bioglass synthesis.

Image 1: Image of the obtained gel

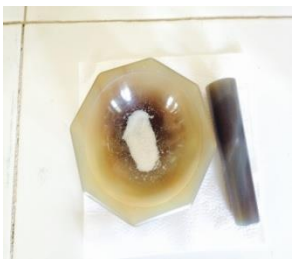

Image 2: Image of the Obtained powder

range [400 to 4000 cm^{-1}] with 4 cm^{-1} resolution and analyzed with opus software.

Their thermal stability were measured using a Thermo Gravimetric and Differential Thermal Analysis technique, which was carried out using Q5000 thermo-gravimeter (TA instrument) with (DSC/TG) analyzer and a sensitivity of 0.1 µg,. In all measurements the weight changes in the material as a function of temperature under 50 sccmAr-gas flow in order to avoid any reaction of the material to be studied with the atmosphere of the furnace. The temperature was increased from room temperature to 1000 °C with a heating rate of 10 °C/min. It makes the possibility to determine the phase transitions: the glass transition temperature (Tg) of polymers, metallic glasses and ionic liquids; melting and crystallization temperatures; the enthalpies of reaction, to know the cross-linking rates of certain polymers.

The products morphology were also analyzed by a Field Emission Scanning Electron Microscopy (FESEM) technique (JEOL 6700-FEG microscope) operating at 3 kV equipped with an Energy dispersive X-ray spectroscopy (EDX) component which help to the determination of the chemical composition (quantitative analysis) in order to control the multi-structures quality, purity and dimension. For the FESEM analysis, the products were fixed directly on the sample holder by a graphite paste..

III. Results and Discussion

The qualitative characterization of the synthesized SiO_2-CaO-P_2O_5 bioglass was carried out using different methods such as X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to study their structural and morphological properties of these products obtained by sol-gel method through the precursor ratio variation and the drying mode.

Also, the thermal properties of these synthesized glass gel materials were studied using thermogravimetry and differential thermal analysis (ATG / ATD) after dehydration.

A. Effect of drying mode (open or closed)

Table 1 shows the different proportions of aerosil precursors and calcium nitrate terahydrate in the synthesized samples with the open and closed drying mode.

Table 1: Percentage of precursors and drying mode

Samples	SiO_2 (mol. %)	$CaNO_3.4H_2O$ (mol. %)	Drying mode
AH I-1	50	50	Open
AH I-2	50	50	Closed
AH II-1	70	30	Open
AH II-2	70	30	Closed

Figures 2 and 3 show the diffractograms and the FTIR spectra of the obtained samples after open and closed drying modes, respectively. The open drying mode (AH I-1 and AH II-1) gave us a hard component, whereas the closed mode (AH I-2 and AH II-2) led to a dry gel. In addition it is noted that the drying mode does not influence the structural behaviour.

Figure 2 shows the DRX diffractograms of the four samples treated at 600 ° C. Note the typical broad band around 22.6 °, meaning the amorphous character of silica-based materials as reported previously [5].

However Figure 3 illustrates the results of the FTIR spectra that are resumed as follows:

The wide band between 3383 and 3463 cm-1 is due to the stretching vibration of the O-H bond from the silanol (Si-OH)

groups and the HO-H vibration of the adsorbed water molecules.

The small band between 1631 and 1740 cm-1 is attributed to the flexural H-OH bond of adsorbed water molecules. The large bands at 1078 and 1093 cm-1, are assigned respectively, to the symmetric and asymmetric stretching modes of the SiO_4 tetrahedrate, while the small band at 797 cm-1 is caused by the Si-OH group [6,7].

We can see clearly the effect of the two principal synthesis parameter (drying mode and precursor's composition) on the bands wave numbers shifting.

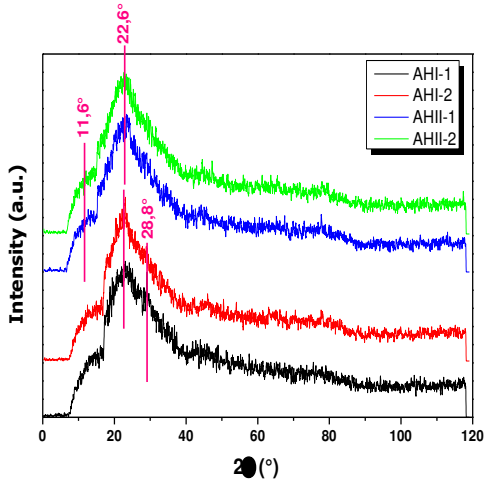

Figure 2: DRX diffractograms of the samples obtained after an open (AH I-1 and AH II-1) and closed (AH I-2 and AH II-2) drying mode of the synthesized gel.

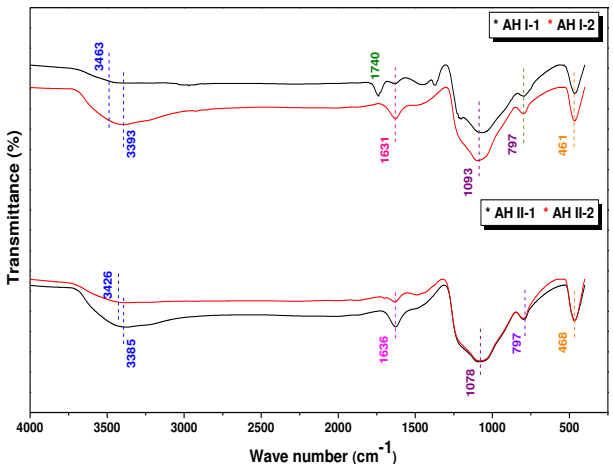

Figure 3: FTIR spectra of samples obtained after open and closed drying.

B. Effect of Precursors Ratios

In order to follow a correct interpretation of the thermal behavior and the FTIR spectra, we have carried out samples of glass gel subject to this study (with Ca / P molar ratio of 4.4% and 1.7%), using the starting material containing CaO and SiO_2 in molar percentages of 50 mol% of each one.

In the interest of obtaining a stoichiometric mixture, the ratio of the precursors: the aerosil SiO_2, calcium nitrate tetra-hydrate ($CaNO_3.4H_2O$) and sodium hydrogenphosphate (Na_2HPO_4), used was varied and the selected percentages of the precursors are reported in the following table (Table 2).

Table 2: Ratio of precursors used for the synthesis of "SiO_2-CaO-P_2O_5" bioglass

Precursors Samples	SiO_2 (mol.%)	$CaNO_3.4H_2O$ (mol. %)	Na_2HPO_4 (mol. %)
Sample/I	50	50	0
Sample/II	73	22	5
Sample/III	73	17	10

B.1 Structural investigation

We firstly started by identifying our products synthesized by the Sol-Gel method using X-ray diffraction. Figure 4 shows their diffractograms of three different precursors used in Ca and P, according to Table 2.

These diffractograms recorded after the calcination step confirm a reorganization of the network which occurs as a function of the calcinations temperature as reported in the literature [8]. In particular, the diffractograms of the three samples, treated at 600°C, have a typical broad band of materials around 22.9°, characterising the amorphous character of silica-based materials [9].

In order to confirm the results obtained by (XRD), we also carried out an analysis by FTIR spectroscopy to determine the kind of bonds present in each product obtained after the calcination step. Figure 5 shows the FTIR spectra of the three different precursors employed in Ca and P [10].

This analysis shows the presence of four main bands at 1471 cm^{-1}, 1060 cm^{-1}, 1627 cm^{-1} and 3448 cm^{-1}. The presence of SiO_2 as the main phase is proved by the wide bands at 1060 cm^{-1} and narrow at 788 cm^{-1}, attributed respectively to, the

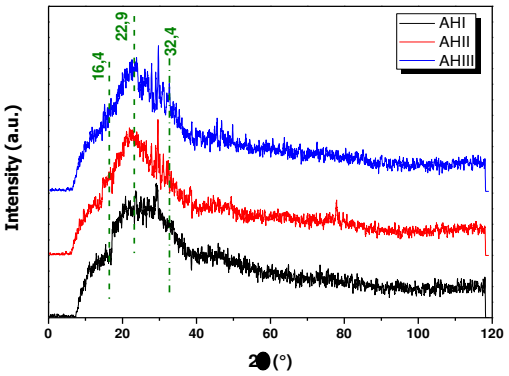

Figure 4: The diffractograms of the samples recorded with different stoichiometry after the calcination step.

symmetrical stretching modes of the SiO_4 tetrahedra and SiOH group. The high Ca^{2+} content also causes the formation of a band at 1471 cm^{-1} [11].

However, the bands around 564 cm^{-1} and 611 cm^{-1} are due to the asymmetric stretching vibrations of the PO bond where the PO_4^{-3} ion and the overhead indicates the number of oxygen bridging bonds formed with other ions PO_4^{-3}, which confirms the presence of tricalcium phosphate (TCP) and calcium phosphate silicate [Ca_{15} $(PO_4)_2$ $(SiO_4)_6$] [12].

The broad band around 3448 cm^{-1} is due to the stretching vibration of the OH bond from the silanol (Si-OH) groups and the HO-H vibration of the adsorbed water molecules. The small band at 1627 cm^{-1} is attributed to the flexural H-OH bond of absorbed water molecules. These bands were present

in the calcined samples because the water molecules were unable to escape from the silica matrix.

B.2 Thermal behavior investigation

Moreover, thermal behavior has been studied using the thermal analysis curves and the differential thermal analysis (TGA / DTA): These curves carried out under inert gas of all synthesized materials are represented in Figure 6. These obtained results firstly confirm the complete conversion of precursors used such as calcium nitrates to calcium oxide CaO in all samples treated at 600°C during the two hours; which confirms that it is a sufficient temperature to have these oxides. Table 3 shows the characteristics obtained from these thermal analysis curves, which were calculated by the OriginLab software.

Moreover from Figure 6, all calcined samples undergo a two- to three-stage processes with corresponding total mass losses in the range 11-14 wt% with two consecutive reactions. The first and the essential is due to a simple dehydration around 130°C. Since this process can be considered approximately as it was possible to apply a kinetic procedure of the mass loss derivatives, for the purpose of verifying the different reactions that have occurred. Despite the very similar thermal behavior of all samples, some differences in the kinetics of water release can be highlighted (See Figure 5 on the bottom). The second step takes place between 150 and 600°C, corresponding to mass losses between 16 and 20 wt%. This step, which turns out to be the glass transition temperature, appears to be correlated with the amount of P_2O_5 in the material; i.e. the higher P_2O_5 content, the greater the loss of mass [13]. Furthermore, it appears to be observed within this temperature range, a possible decomposition of

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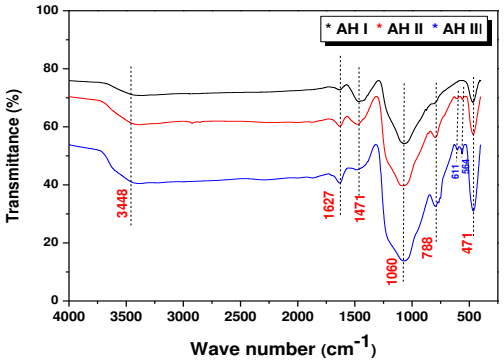
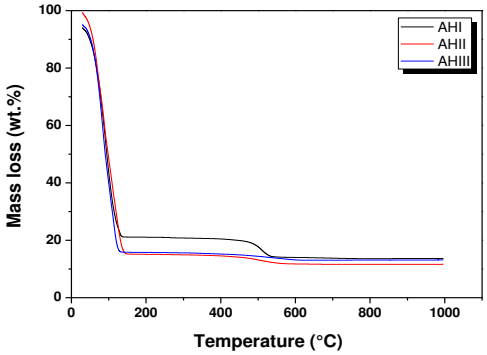


Figure 5: Infrared Spectroscopy (FTIR) of the samples obtained after the calcination step.



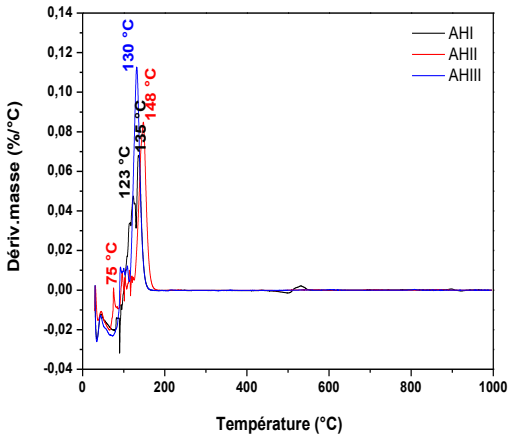


Figure 6: The curves of the gel glasses studied in the Ar atmosphere (50 ml / min) at 10° C.min-1.

the nitrates and the formation of CaO. The third stage from 600 to 1000°C results in a stationary behavior; where the stability is reached at 600°C as glass transition temperature (Tv = 600°C) [14].

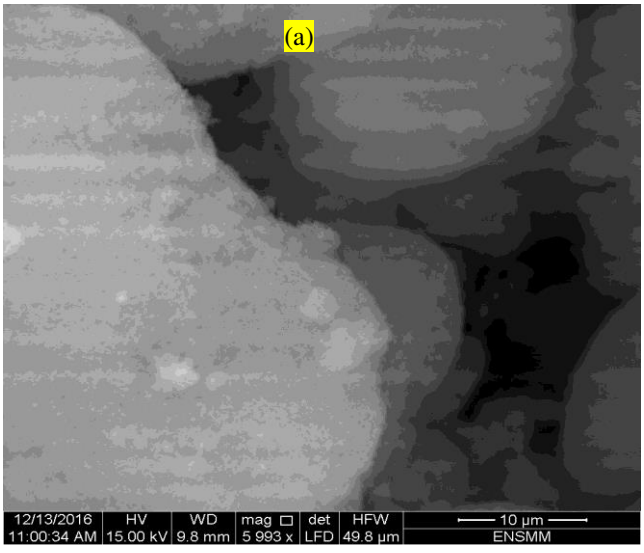
Table 3: Loss of mass deduced from the thermal analysis of "SiO_2-CaO-P_2O_5" synthesized bioglass

Mass loss	Total (wt.%)	Peak (°C)
Sample/I	**13,5**	**135**
Sample/II	**13,2**	**148**
Sample/III	**11,6**	**130**

B.3 Morphological investigation

In addition, a qualitative analysis of these synthesized bioglass was carried out by FE-SEM and their micrographs are showed in Figures 7 and 8.

Figure 7 shows FESEM micrographs of the synthesized bioglass prior the heat treatment or calcinations step. With a magnification of **10 µm** and an accurate view at **4µm**, the structure seems to be compact and the inhomogeneity is not present.



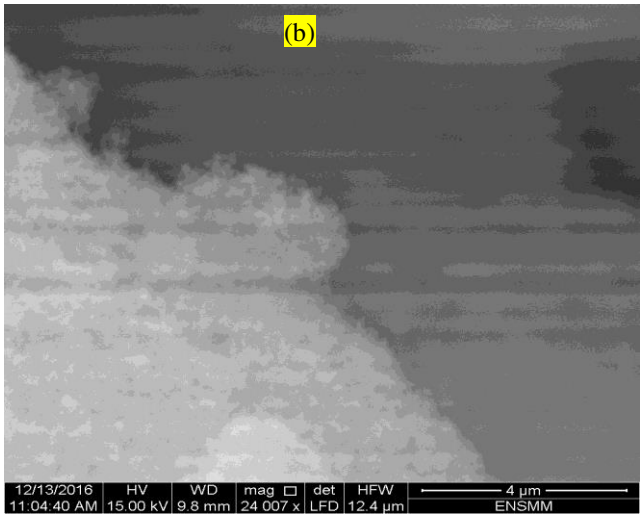


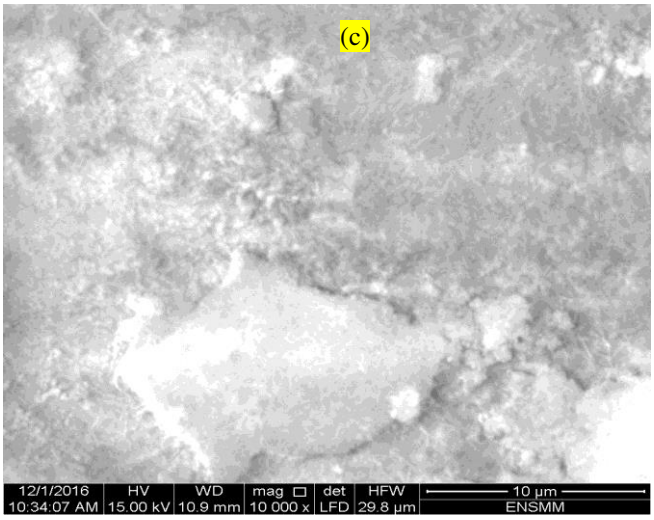
Figure 7: FESEM micrographs of bioglass before calcination step at 600 °C.

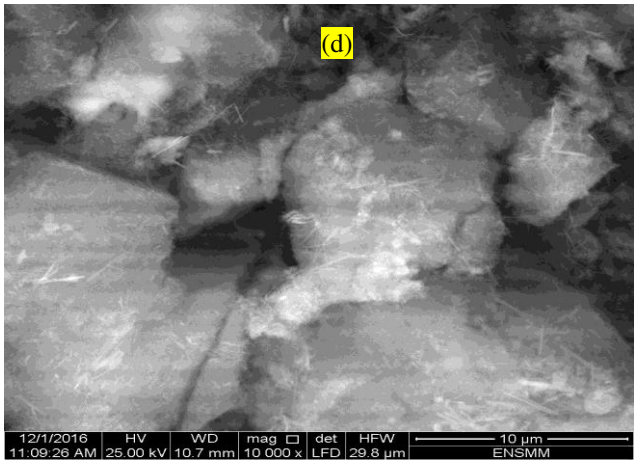
The morphological analysis of the surface area of the treated bio-glass at 600°C, shows that these synthesized glasses synthesized by the sol-gel process are inhomogeneous on the surface of samples I, II and III. There is an appearance and a composition of nanofibers forming together plate-like amorphous form structures, as shown in Figure 8; with a magnification of 10 µm for the three samples **[(A), (B) and (C)], and 5µm for sample III (D)**. It can be deduced that the addition of P_2O_5 into samples II and III leads to the formation of a structure of a solid cluster surrounded by very porous nanofibers in the form of a plate is more apparent with respect to sample I, of the filaments in the form of eels [15,16].

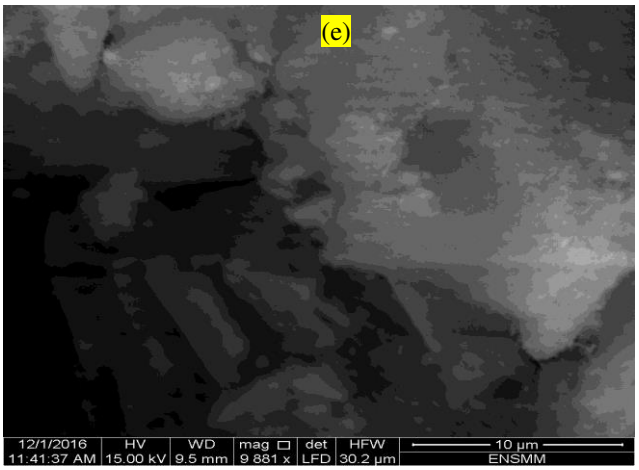
IV. Conclusion

In this paper, a synthesis of three gel-glass materials based on the ternary system SiO_2-CaO-P_2O_5 using simple and low sol-gel method, with different compositions was proposed. A multi-analysis technique was considered as a complete structural and morphological characterization of these synthesized nanocomposites.

The chemical and structural characterization showed that the heat treatment induced clearly a modification on the biomaterial. However, it remains to confirm their promising applications. This obtained bioglass can have several applications in sustained – release drugs and bone filling.







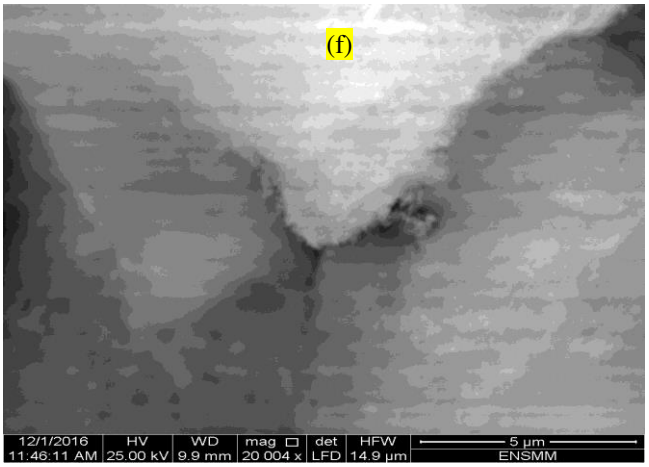


Figure 8: FESEM micrographs of the bio-glass obtained after calcination at 600°C.

Therefore, from these obtained results, it can be concluded that:

1- The formation of the SiO_2, CaO and P_2O_5 bioglass nanocomposite is reached in the temperature range between 150°C and 600°C.

2- The temperature of the glass transition is found to be around 600°C.

3- The addition of P_2O_5 influenced the structure of the bioglass by creating the pores.

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Author Biographical notes:

Aymen Hadji is currently assistant specialist in pharmaceutical mineral chemistry working in Souk Ahras Hospital (Algeria) and a member of the research team renewable energies in the Mathematical Modeling and Numerical Simulation Research Lab. He was a specialized doctorate student in the Laboratory of Pharmaceutical Mineral Chemistry, Faculty of Medicine, Badji-Mokhtar University, Annaba-Algeria. He is working on bio-glasses and their medical applications. He has also been involved in UK-Qualitative Systems Pharmacology study groups with several research reports and a published paper on bispecific antibodies. https://www.researchgate.net/profile/Aymen_Hadji

Abdelali Merah is a senior lecturer in the Laboratory of Pharmaceutical Mineral Chemistry, Faculty of Medicine, Badji-Mokhtar University, Annaba-Algeria, working on pharmaceutical mineral chemistry. He published many papers on this subject.
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Ounassa Guellati is a lecturer in the physics department, Mohamed Cherif Messadia University-Souk Ahras, , and a researcher in LEREC Laboratory, Faculty of Sciences, Badji-Mokhtar University, Annaba-Algeria. She has been working in nanotechnology on nanostructured material production and physico-chemical properties for different applications such as: Environnement, Energy storage and biosensing. She published many papers.
https://www.researchgate.net/profile/O_Guellati

Mohamed Guerioune is a Professor in the physics department, Faculty of Sciences, Badji-Mokhtar University, Annaba-Algeria, and the director of LEREC Laboratory. He published more than 40 papers on nanostructures and nano composite. He has also been granted an international prize for a novel research in "technology innovation" in 2012.
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