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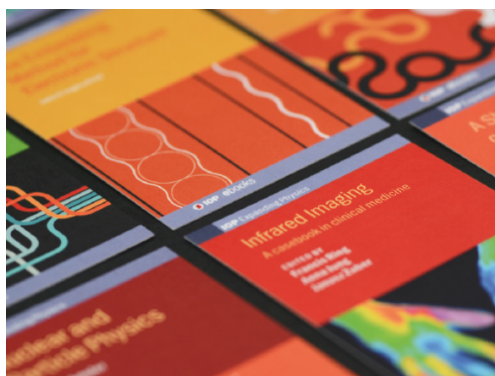
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Characterization of bismuth-silicate soles

J Bautista-Ruiz¹, A Chaparro², and W Bautista³

¹ Universidad Francisco de Paula Santander, San José de Cúcuta, Colombia

² Universidad ECCI, Bogotá, Colombia

³ Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia

E-mail: jorgebautista@ufps.edu.co

Abstract. The bismuth silicate compound was synthesized by the sol-gel method from bismuth nitrate pentahydrate and tetraethoxysilane, as precursors. The sol-gel method is attractive because the processes for obtaining oxides are developed at room temperature. In addition, it allows precise control over the composition, homogeneity, and deposition of coatings. The impact of bone-related diseases and trauma has increased significantly, in recent decades in developed and developing countries. There are materials such as bioactive glasses, especially silica compounds, which are called to play a very important role in this area, due to properties such as osteoconductivity, osteoproduction, and osteoinduction. For 20 years, the sol-gel method and the supramolecular chemistry of surfactants have been incorporated into the field of bioceramics, which allows the control, on a nanometric scale, of porosity in bioglasses. The sol-gel method has allowed obtaining bioactive materials with high surface area and high porosity. The study consisted of shaping soles by varying the molar concentrations of tetraethoxysilane and assessing the effect on aging, viscosity, determining the presence of specific functional groups and establishing the transformations that take place as a function of temperature. The results allowed characterizing each of the sol for possible application in bioglasses.

1. Introduction

The sol-gel process as a chemical synthesis method allows the conformation of ceramic materials from polymerization routes of components in liquid state, sol, at room temperature [1]. The sol is defined as a stable suspension of colloidal solid particles in a liquid. The colloidal particles that form it, denser than the liquid medium that surrounds them, must be very small to avoid precipitation, being suspended by the repulsion of weak forces, such as those of Van der Waals. This condition is fulfilled by particles with sizes between ~1 nm and ~100 nm, corresponding to a density of 10^3 to 10^9 atoms per particle. A gel is a porous solid formed by three-dimensional interconnected chains extended and thermodynamically stable through a liquid medium [2]. In the last two decades, research is being conducted on the benefits that materials such as bismuth and its alloys can offer. A multitude of applications in technology has been found due to its low melting point. Most bismuth is used to form compounds, mainly aluminum and lead. Because their melting points are very low, they are used in special welding, automatic sprinkler meltable parts, safety seals for compressed gas cylinders, and in automatic electric and gas water heater driers. Bismuth has had a growing commercial importance, is not considered toxic and presents a minimum threat to environment [3-9].

Compounds with formula $\text{Bi}_{12}\text{MO}_{20}$ ($\text{M} = \text{Si, Ge, Ti, Pb, Mn B}_{1/2} \text{P}_{1/2}$), called sillenites which can be considered as promising materials for the development of low-temperature co-fired ceramics technology



(LTCC). Sol-gel synthesis offers potential advantages over traditional solid-state synthesis methods because it allows precise control over composition, homogeneity and deposition of coatings [10,11].

The impact of bone-related diseases and trauma has increased significantly, in recent decades in developed and developing countries. There are materials such as bioactive glasses, especially silica compounds, which are called to play a very important role in this area, due to properties such as osteoconductivity, osteoproduction, and osteoinduction. For 20 years, the sol-gel method and the supramolecular chemistry of the surfactants have been incorporated into the bioceramics field, which allows the control, on a nanometric scale, of the porosity in the bio-glass. This advance has promoted a new generation of bioactive glasses obtained by sol-gel with applications in drug delivery systems, as well as in regenerative grafts with good bioactive behavior. In addition, the combination of silica-based glass by adding organic components led to the obtaining of new organic-inorganic hybrid materials with improved mechanical properties. Finally, an effort has been made to organize the preparation of sun-gel glasses at the macroscopic level. This effort has given rise to new macroporous supports, suitable for use in tissue engineering techniques or pieces as porous to be implanted in situ [12]. On the other hand, the osseointegration of Ti implants is widely recognized. However, silicon deficiency in animals leads to bone defects, since this element plays an important role in bone metabolism. Therefore, hybrid synthesis of sol-gel (organic-inorganic) coatings has been performed to create a material capable of releasing silicon compounds under in vivo conditions, to promote rapid and good osseointegration [13]. However, the rational design of mesoporous materials for biomedical applications implies a nanometric scale control. By comparing conventional sol-gel glasses with mesoporous glasses, it is possible to know the progress in research on the subject of biomaterials: the synthesis of conventional sol-gel glasses has allowed us to obtain bioactive materials with a certain surface area and volume total porous [12]

This research proposed as an objective, to produce new knowledge related to the synthesis of the bismuth-silicate (BSO) compound by means of the Sol gel method from bismuth (III) nitrate pentahydrate and tetraethoxysilane (TEOS), as precursors. The study consisted in forming three sols by varying the molar concentrations of TEOS. The characterization focused on: 1) evaluating the aging processes of the sols by monitoring the evolution of viscosity, 2) determining the presence of specific functional groups by Fourier-transform infrared spectroscopy (FTIR), and 3) determining the amount of heat that absorbs or releases each of the sols and identify the type of transformation that takes place according to a certain temperature by means of differential scanning calorimetry (DSC). The results allowed characterizing each of the sol for possible application in bioglasses.

2. Materials and methods

2.1. Reagents

The reagents used for the synthesis of the BSO (bismuth-silicate) sols are listed in Table 1.

Table 1. Features of the reagents used.

Alcoxide	Purity/concentration (%)	Molecular weight (g/mol)	Density (g/cm ³)
Tetraethoxysilane - Si(OC ₂ H ₅) ₄	98	208.33	0.93
Bismuth (III) nitrate - Bi(NO ₃) ₃ 5H ₂ O	98	485.07	2.83
Acetic acid - C ₂ H ₄ O ₂	100	60.05	1.05
Ethanolamine - C ₂ H ₇ NO	98	61.08	1.01
2-Ethoxyethanol - C ₄ H ₁₀ O ₂	98	90.12	0.93

2.2. Bismuth silicate synthesis

In this synthesis, the methodology proposed by Veber, *et al.* is adapted [14]. Initially, the amount of pentahydrate bismuth nitrate is dried for 96 hours at 65 °C in a vacuum oven, whose purpose is to decrease the amount of water in the system. A solution is prepared with the dehydrated bismuth nitrate dissolved in acetic acid and left in magnetic stirring for 2 hours. Another solution is prepared with TEOS and 2-ethoxyethanol and left in magnetic stirring for half an hour. 2-ethoxyethanol is the solvent for

TEOS. For this work, the molar concentrations of TEOS were: 0.75; 0.90 and 1.05. These relationships were based on research developed by Veber, *et al.* [14]. After the agitation time of the two solutions has elapsed separately, they are mixed and left in magnetic stirring for three more hours. At this point, with ethanolamine, the pH is adjusted to a value of 4. In Figure 1, the synthesis process is shown schematically, with the respective stages and times employed in each of them.

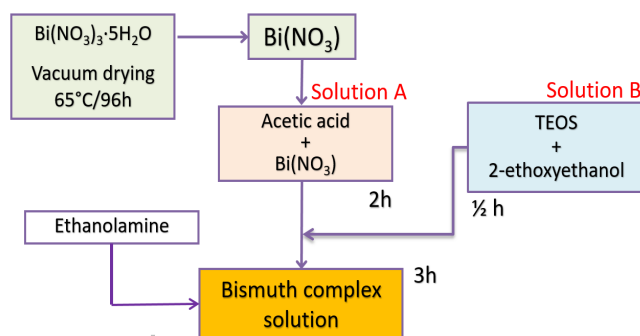


Figure 1. Synthesis for soles of BTO system.

Table 2 and Table 3 show the amount of precursors used for the synthesis of BSO sols, varying in the concentration of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Bi}(\text{NO}_3)_3$ precursors in the system and using $\text{C}_2\text{H}_7\text{NO}$ as a complexing agent. This variation allowed to determine the effect that the concentration of the silicon precursor has when evaluating the evolution characteristics of the sol.

Table 2. TEOS molar concentrations.

Sols	Concentration
M1	0.75
M2	0.90
M3	1.05

Table 3. Amount of reagents used for the BTO system.

Molar ratio	$\text{Si}(\text{OC}_2\text{H}_5)_4$ (ml)	$\text{C}_4\text{H}_{10}\text{O}_2$ (ml)	$\text{Bi}(\text{NO}_3)_3$ (g)	$\text{C}_2\text{H}_4\text{O}_2$ (ml)
M1		5.27		
M2	0.38	14.78	10	25
M3		7.80		

2.3. Characterization equipment

To measure the viscosity, a Cannon-Fenske routine capillary viscometer with a range between 0.8 cSt and 8 cSt was used. DSC thermograms were obtained using a TA Instruments Q20 differential scanning calorimeter. Heating rate of 5 min^{-1} in the range of $25 \text{ }^\circ\text{C}$ to $315 \text{ }^\circ\text{C}$. The sample is purged with N_2 at a flow rate of 50 ml min^{-1} . The sample size ranged from 4 mg to 8 mg. For FTIR a Thermo NicoletTM device, model FTIR iSTM10 was used. The working conditions were: infrared from 400 cm^{-1} to 4000 cm^{-1} , transmittance mode, Resolution 0.4 cm^{-1} and number of scans equal to 32. OMNIC work software.

3. Results and discussions

3.1. Viscosity

When the sol increases viscosity (aging), hydrolysis and condensation reactions within the system occur; These give origins to polynuclear species that form bonds generating an internal structure and giving a medium rigidity to the system. To study the development of these reactions over time the measurement of the viscosity of the system is used. Figure 2 shows the kinematic viscosity curves as a function of time for the BSO system according to the molar ratios M1, M2 and M3 respectively. The curves show

how gelation time varies with increasing concentration of TEOS, the precursor of silicon, in the sols studied.

In the curves presented in Figure 2 the stability of the sols is evident; it can also be concluded that it takes several weeks for the gelation of the system to begin. The gelation occurs slowly, for several weeks, and eventually develops quickly. The gelation time is determined by the moment in which the viscosity of the system undergoes an appreciable change in its value with respect to the values previously measured; in the curve corresponds to the loss of horizontality in it (first appreciable change in the slope of the curve).

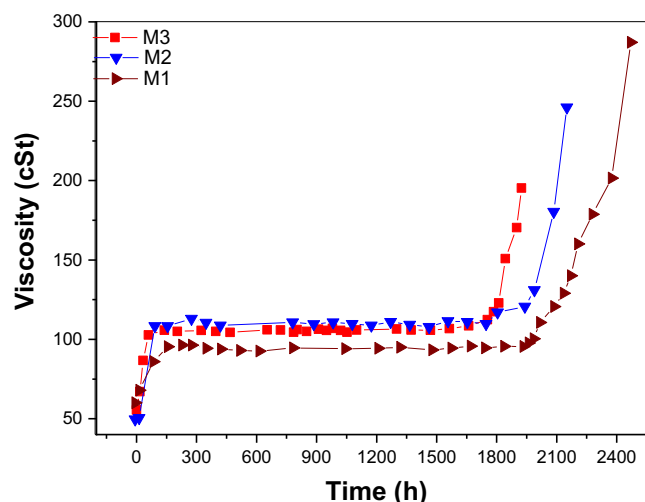


Figure 2. Viscosity curves of the BSO system.

In the system, the concentration of the silicon precursor determines the gelation time of the sols, as the silicon concentration increases the gelation time decreases. This is evidenced by the viscosity curves of Figure 2 and the information recorded in Table 4.

Table 4. Gelation times of the sols of the BSO system.

Molar concentration	Gelation times (h)
M1	2000
M2	2200
M3	2500

From Figure 2, we observe the tendency of the sol bismuth - silicate to be gelled by the changes in the viscosities of the system, modifications that allow dividing the aging process of the sol into three regions: a) the zone 1 where the viscosity undergoes considerable changes, b) zone 2 where the viscosity value is stabilized and c) zone 3 when the viscosity increases rapidly from one day to the next, it is at this stage that the system gels. In Table 5, the regions of each sun corresponding to its studied molar concentration are specified.

The evolution of the viscosity of the system is an important variable to consider since it is directly related to the thickness of the bioglass or biocompatible coating deposited on the substrate. The results allow defining the required thickness in the bioglass considering that high viscosities generate greater thicknesses although this does not guarantee that the coating is homogeneous and free of cracks. For this reason, it is necessary to study the evolution of the systems and establish what is the optimum viscosity value at which the bioglasses should be obtained according to the specific application.

It is very important to distinguish the three regions in the viscosity curves as a function of time as the shaping of the coatings is relevant viscosity of the soles and the choice of a suitable viscosity largely defines the good features in texture, microstructure and homogeneity of the layers or bioglass conformed.

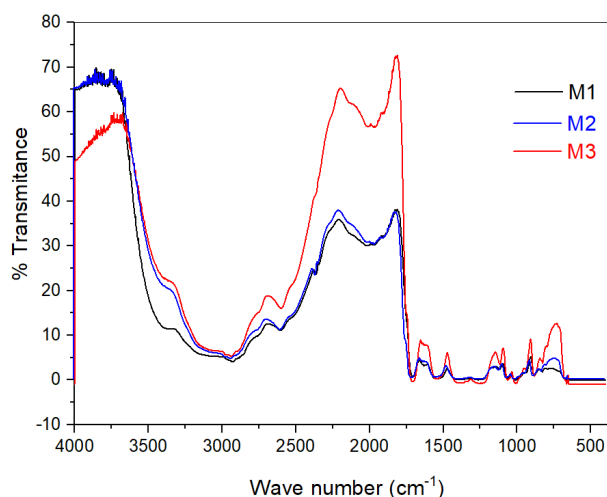
Table 5. Viscosity zones of the soles BSO system.

Concentration	Zone 1		Zone 2		Zone 3	
	Time (h)	η (cSt)	Time (h)	η (cSt)	Time (h)	η (cSt)
M1	0 – 160	60 – 95	160 -1940	94 – 95	> 1940	> 290
M2	0 – 200	50 – 110	110 -1800	110 – 112	> 1800	> 250
M3	0 – 100	55 – 105	100 -1600	2 – 3	> 2000	> 195

3.2. Fourier transform infrared spectroscopy

Identifying the types of bonds present in the sol of the bismuth-silicon system is necessary because it allows knowing the reaction rates and equilibrium constants of the compound. This information establishes the specific positions of the bands to determine the presence of intermolecular hydrogen bonds and structural differences between isomers and conjugates of the bismuth-silicon compound (Figure 3)

Experimentally it is observed in Figure 3, of the mixture of the substances to produce the suns, a composite absorption curve corresponding to the sum of the individual constituents that make up each sun is obtained. Furthermore, it is found that certain absorptions represent a measure of the concentration of the compounds in the mixture.

**Figure 3.** FTIR spectra of the BSO system.

In Figure 3, the FTIR spectra are shown for the three studied concentrations of the BSO system. Localized bands are exhibited at 1670 cm^{-1} and 1288 cm^{-1} , which are ascribed to the symmetric and asymmetric vibrations of the C=O bonds of the —CH_3 groups and coordinated monodentates for the bismuth. The bands at 1575 cm^{-1} and 1490 cm^{-1} are attributed to asymmetric vibrations ($\nu_s(\text{COO}^-)$) and symmetric vibrations ($\nu_a(\text{COO}^-)$), which are bidentate coordinated for the bismuth ion. The absorption band at 1087 cm^{-1} is attributed to the voltage vibration Si—O—Si [4]. The bands near 3421 cm^{-1} and 947 cm^{-1} correspond to the free butanol formed during the chemical reaction, specifically $\nu(\text{OH})$ and $\nu(\text{CO})$. The two bands around 1500 cm^{-1} can be assigned to vibrations of the CH_3COO group, $\nu(\text{CO}_2) = 1545\text{ cm}^{-1}$ asymmetric and $\nu(\text{CO}_2) = 1444\text{ cm}^{-1}$ symmetric [15].

The bands close to 3421 cm^{-1} and 947 cm^{-1} correspond. The peaks that appear at 2980 cm^{-1} and 2875 cm^{-1} are due to the voltage vibration of the alkyl groups. Tension vibrations for Bi—O and O—Si—O bonds appear at 472 cm^{-1} and 1082 cm^{-1} tendency of the formation of tetrahedron SiO_4 and bonds Bi—O—Si [16]. The bands between 1800 cm^{-1} and 1770 cm^{-1} correspond with vibrations of extension of the C=O groups. To weak vibrations of the link $\text{C}\equiv\text{N}$ [17].

Table 6 shows the location of the bands in the spectrum of Figure 3 and the corresponding assignment to certain functional groups.

Table 6. Infrared absorption of the BSO system.

Assignment	Wave number (cm ⁻¹)
ν O-H	3412
ν_a C-H in CH ₃	2955
ν_s C-H in CH ₃	2930
ν_a C-H in CH ₂	2880
Vibrational mode ν (C=O)	1535
ν CH ₃	1361
Combined mode ν (C-CH ₃) + ν (C=C)	1283
Stretch Si-O in Si-O-Si units	1180
ν_a (Si-O-Si)	785

3.3. Differential scanning calorimetry

In Figure 4, the graphs corresponding to the characterization by the DSC technique of the soles of the BSO system in their three study concentrations are shown. A peak is observed below 215 °C related to the removal of volatile water residues [10], acetic acid and ethanolamine, associated with a weak endothermic peak around 60 °C. The exothermic peak present around 215 °C is most likely due to the pyrolysis of the same organic compounds present in the suns [10], that is, the chemical decomposition of organic matter and all kinds of materials, except metals and glass, caused by heating at high temperatures in the absence of oxygen.

Differential scanning calorimetry is a dynamic experimental technique that allows determining the amount of heat absorbed or released by a substance, when it is kept at a constant temperature, for a certain time, or when it is heated or cooled at a constant speed, in a certain interval of temperatures.

Among the various utilities of the DSC technique, the following stand out: measures of apparent heat capacity (structural relaxation phenomena). Determination of transformation or transition characteristic temperatures such as vitreous transition, ferro-paramagnetic transition, crystallization, polymorphic transformations, fusion, boiling, sublimation, decomposition, isomerization, etc. Thermal stability of the materials. Kinetics of crystallization of materials.

The results obtained allow the design of the heating program for the synthesis of bioglass or biocompatible films.

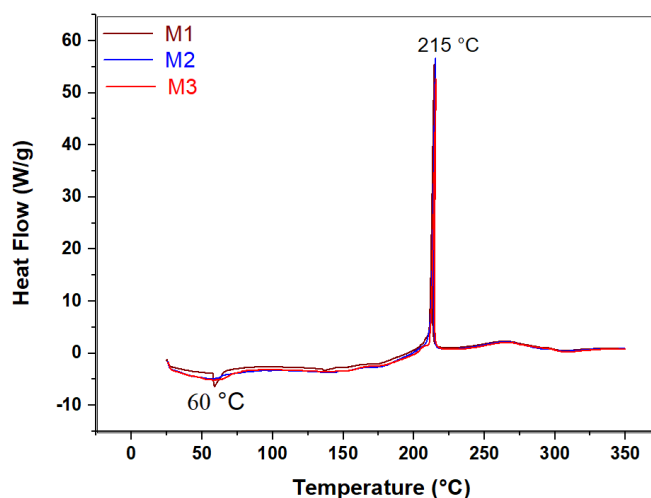


Figure 4. DSC curves of the BSO system.

4. Conclusions

The study of the three concentrations concludes: 1) The stability of the sols, BSO, catalyzed in acid medium, extends for several weeks until they begin to gel; this can be concluded by observing the curves that indicate the variation of the viscosity of the sols over time. 2) FTIR results identified the types of bonds present in the sols, especially tension vibrations for Bi—O and O—Si—O bonds at 472 cm^{-1} and 1082 cm^{-1} tendency of the formation of tetrahedron SiO_4 and bonds Bi—O—Si. 3) The results of DSC, allow establishing the sintering program for the manufacture of bio-glass, with low heating rates and permanence at temperatures of $65\text{ }^\circ\text{C}$ for evaporation of solvents and at $215\text{ }^\circ\text{C}$ to consolidate the samples.

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References

- [1] Bautista-Ruiz J, Aperador W, Delgado A and Díaz-Lagos M 2014 *International Journal of Electrochemical Science* **9** 4144
- [2] Brinker C and Scherer G 1993 *Materials & Manufacturing Process* **8(3)** 391
- [3] Kartavtseva M 2007 *Thin Solid Films* **515** 6416
- [4] Rohr O 2002 *Ind. Lubr. Tribol.* **54** 153
- [5] Zhu H, Hu J, Zhang Y and Fei Y 2009 *Advanced Tribology* **3** 878
- [6] Bautista-Ruiz J, Ruiz E, Duque J, Aperador W and Olaya J 2016 *Int. J. Chem. Sci.* **14** 1447
- [7] Mackenzie J and Bescher E 2000 *Journal of Sol-Gel Science and Technology* **19** 23
- [8] Kang C and Lee Y 2012 *Journal of industrial and Engineering Chemistry* **18** 1670
- [9] Balamurugan A, Kannan S and Rajeswari S 2005 *Materials Letters* **59** 3138
- [10] Veber A, Kunej S, Cerc R and Suvoriv D 2020 *Journal of the European Ceramic Society* **30** 2475
- [11] Gua H, Dongb C, Chena P, Kuanga A and Lic X 1998 *Journal of Crystal Growth* **186** 403
- [12] Arcos D and Vallet-Regí M 2010 *Acta Biomaterialia* **6** 2874
- [13] Juan-Díaz M, Martínez-Ibáñez M, Lara-Sáez I, Silva S, Izquierdo R, Gurrunchaga M, Goñi I and Suay J 2016 *Progress in Organic Coatings* **96** 42
- [14] Veber A, Kunej S and Suvorov D 2010 *Ceramics International* **36** 245
- [15] Sánchez C, Livage J, Henry M and Babonneau 1998 *Journal of Non-Crystalline Solids* **100** 65
- [16] Zhu X, Xie j, Lin D, Guo Z, Xu J and Shi Y 2014 *Journal of Alloys and Compounds* **582** 33
- [17] Bautista-Ruiz J, Aperador W and Caicedo J 2018 *Indian Journal of Science and Technology* **11** 1
- [18] Wang S, Li W, Wang S, Jiang J and Chen Z 2016 *Microporous and Mesoporous Materials* **221** 32