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SYNTHESIS AND PRELIMINARY CHARACTERIZATION OF MODIFIED 45S5 BIOGLASSES

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ABSTRACT. The study is devoted to synthesis and preliminary structural and morphological characterization of modified 45S5 glasses, in (66-x)SiO_2·27CaO·4P_2O_5·3TiO_2·xAl_2O_3 system, with potential applications in dentistry. The composition of the sol-gel derived samples was verified with respect to their nominal composition. The effect of partial SiO_2 replacement with Al_2O_3 on samples structure and morphology is investigated. It was established that the Ca/P ratio is diminished in Al_2O_3 containing samples and that an amorphous hydroxyapatite phase similar to hydroxyapatite reported for bone tissue is formed.

Keywords: *bioglasses; sol-gel-synthesis; XRD; SEM; EDX.*

INTRODUCTION

Bioactive glasses and oxide glass components introduced into composite materials represent an important class in biomaterials field with applications in orthopaedics and dentistry [1,2]. When in contact with the body fluid, these materials generate a series of chemical and physical reactions that lead to the formation of hydroxyapatite – the mineral phase of bone tissue. Bone and enamel share the same hydroxyapatite mineral phase, but they differ in morphology and organic content. The composition of enamel is nearly completely inorganic, while bone has a relatively high organic composition. In pure hydroxyapatite, $Ca_5(PO_4)_3(OH)$ - often noted $Ca_{10}(PO_4)_6(OH)_2$, the ratio between the number of calcium and phosphorus atoms is Ca/P = 1.67, while in different bone tissues it differs and takes values encompassed in $1.9 < Ca/P < 2.2$ range and even outside of that [3,4].

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Oxide glasses of SiO_2-CaO-P_2O_5 system are a class of materials with high potential for applications such as bioactive glasses for bone tissue repair, tissue regeneration and other various dental applications [5-10].

An important characteristic of composite materials containing bioactive glass is the proportion of the glass phase which influences the mechanical properties. The elimination of residual stresses and cracks at the microscopic level play a key role in the development of high-strength biomaterials. The term "bioglass" was initially introduced for the glass with the composition 46.1 mol.% SiO_2, 24.4 mol.% Na_2O, 26.9 mol.% CaO and 2.6 mol.% P_2O_5, registered as Bioglass ®, with consecrated denomination as 45S5 bioglass [11]. The partial replacement of Na_2O and CaO with other oxides may improve certain glass properties. For example, the replacement with K_2O and MgO allows the control of expansion coefficient [12,13].

The compositional range of 45S5 bioglass can be enlarged by introducing oxides like TiO_2 and Al_2O_3, which may increase the activation energy of crystallization [14]. Moreover, it was reported that the addition of TiO_2 and Al_2O_3 improves the mechanical properties of glasses and enhances their adherance to bone tissue [15,16].

The aim of this paper was the synthesis and preliminary structural and morphological characterization of modified 45S5 glasses, in $(66\text{-}x)SiO_2 \cdot 27CaO \cdot 4P_2O_5 \cdot 3TiO_2 \cdot xAl_2O_3$ system. At the same time, the composition of the prepared samples was verified with respect to their nominal synthesis composition. The structural and morphological effect of the new glass system as well as the partial SiO_2 replacement with Al_2O_3 is considered of interest for the design of composite biomaterials with potential applications in dentistry.

EXPERIMENTAL

Glasses of $(66\text{-}x)SiO_2 \cdot 27CaO \cdot 4P_2O_5 \cdot 3TiO_2 \cdot xAl_2O_3$ system, with x= 0, 1 and 2 mol% (Table 1), were prepared by sol-gel method, which is largely applied to obtain bioactive glasses [5,6,15,16]. Tetraethyl orthosilicate ($Si(OC_2H_5)_4$ – TEOS), triethyl phosphate ($(C_2H_5)_3PO_4$ - TEP), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), titanium isopropoxide ($(Ti[OCH(CH_3)_2]_4$ - TIP) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were used as precursors of the component oxides. For hydrolysis with HNO_3, the molar ratio (HNO_3 + H_2O) / (TEOS + TEP) was kept 8.

The gelation was achieved after 24 hours by maintaining the solution at 37°C. Then the gels were aged at 37°C for 3 days, and thereafter they were dried at 110°C for 24 hours. Finally, a heat treatment at 600°C was applied for 3 hours, to eliminate the synthesis residues and to obtain a stabilized structure.

Table 1. Notation and nominal composition of the investigated samples

Notation	Composition (mol %)
P_0	$66SiO_2 \cdot 27CaO \cdot 4P_2O_5 \cdot 3TiO_2$
P_1	$65SiO_2 \cdot 27CaO \cdot 4P_2O_5 \cdot 3TiO_2 \cdot 1Al_2O_3$
P_2	$64SiO_2 \cdot 27CaO \cdot 4P_2O_5 \cdot 3TiO_2 \cdot 2Al_2O_3$

The crystallinity of the samples was investigated with Shimadzu XRD-6000 diffractometer using CuKα radiation (λ = 1.54 Å) and Ni filter. The diffractograms were recorded in the angular range $10° \leq 2\theta \leq 80°$ with a speed of 2° / min.

The study of morphology and elemental chemical composition was performed using scanning electron microscopy (SEM) with a Tescan Vega microscope equipped with an energy dispersive X-ray spectroscopy (EDX) detector enabling the assessment of the elemental concentrations in microscopic regions with a spatial resolution of several cubic micrometers.

RESULTS AND DISCUSSION

The X-ray diffraction analysis points out the non-crystalline state of samples after 600 °C treatment. The large diffraction line recorded in a wide angle around $2\theta \sim 26°$ (Fig. 1.a) consists of two components centered at 2θ values of 23.7° and 30.7°, assignable to glass network formers SiO_2 and P_2O_5, respectively. The assignment is supported by the most intense diffraction line of crystalline SiO_2 (JCPDSPDF No. 39-1425) and $Ca_3(PO_4)_2$ (JCPDSPDF No. 17-0498), respectively.

The SEM images of (66-x) SiO2·27CaO·4P2O5·3TiO2·xAl2O3 samples (Figs. 1. b-c) show porous particles with a varied morphology and dimensions between 500 µm and 1 µm, as a result of the agglomeration of particles during the aging process.

On the surface of the larger granules can be observed smaller particles, which may be the result of the rearrangement in a new phase during the heat treatment (Fig.2.a-c-e). The precipitate has acicular or whiskers shapes or they appear as plates.

One notices that the acicular forms are prevalent in P_1 sample. This type of morphology is typical of hydroxyapatite development [17-20]. At the same time, the SEM images indicate the presence of interconnected fine particles that form irregular agglomerations.

EDX spectra collected from the sample's surfaces shown in Fig.2 a-c-e are shown in Fig.2.b-d-f and reflect their chemical elemental composition.

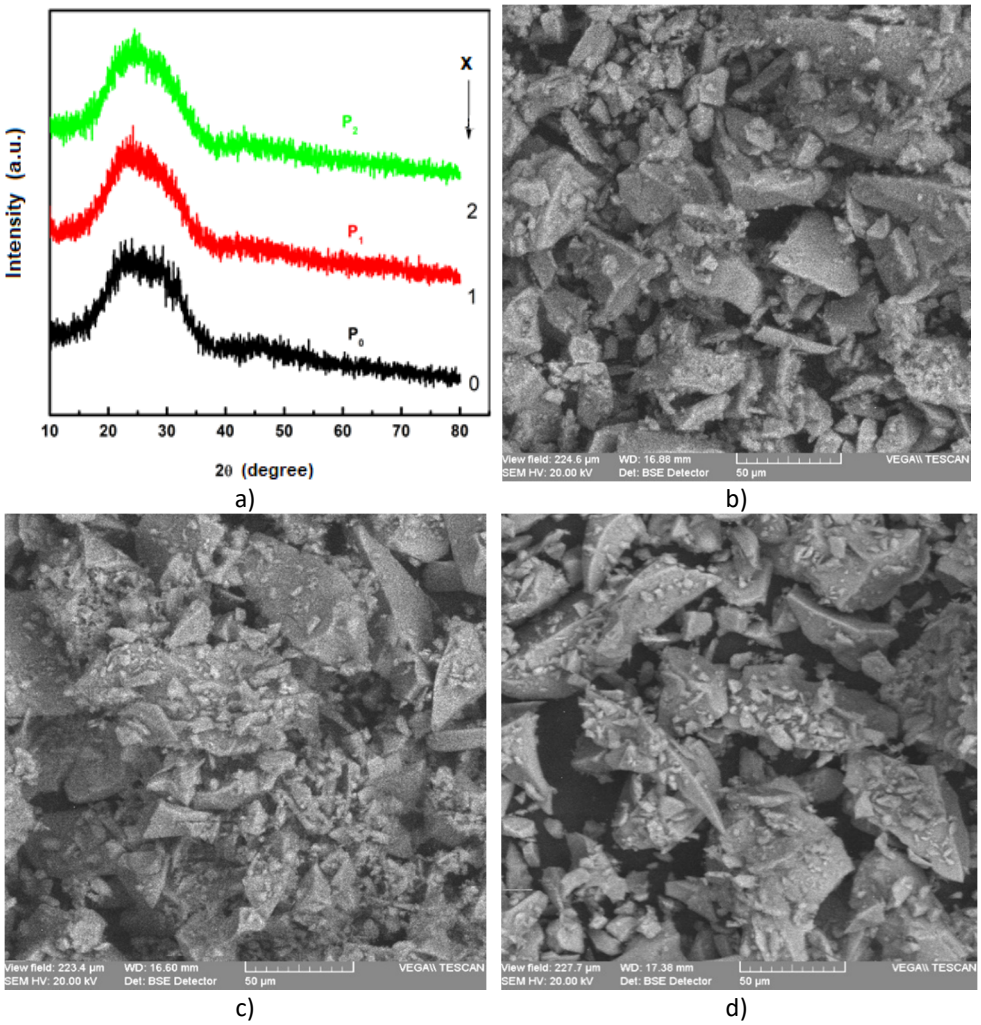

***Fig. 1**. Structure and morphology of glasses in the system (66-x)SiO_2·27CaO·4P_2O_5·3TiO_2·xAl_2O_3: a) XRD patterns; b) SEM image of sample P_0 (x=0); c) SEM image of sample P_1 (x=1); d) SEM image of sample P_2 (x=2).*

The elemental composition of Si, Ca, P, Ti, Al and O elements determined from EDX spectra (Fig. 2) is summarized in Table 2. Deviations from the nominal elemental concentration are observed for Si, Ca and Ti. According to nominal atomic compositions, for all samples prepared under the presented conditions, the Ca/P ratio is 3.375. A close value is obtained for P_0 sample, while for P_1 and P_2 samples, wherein Al_2O_3 was added, the Ca/P ratios are clearly lower, namely 2.03 and 2.63, respectively.

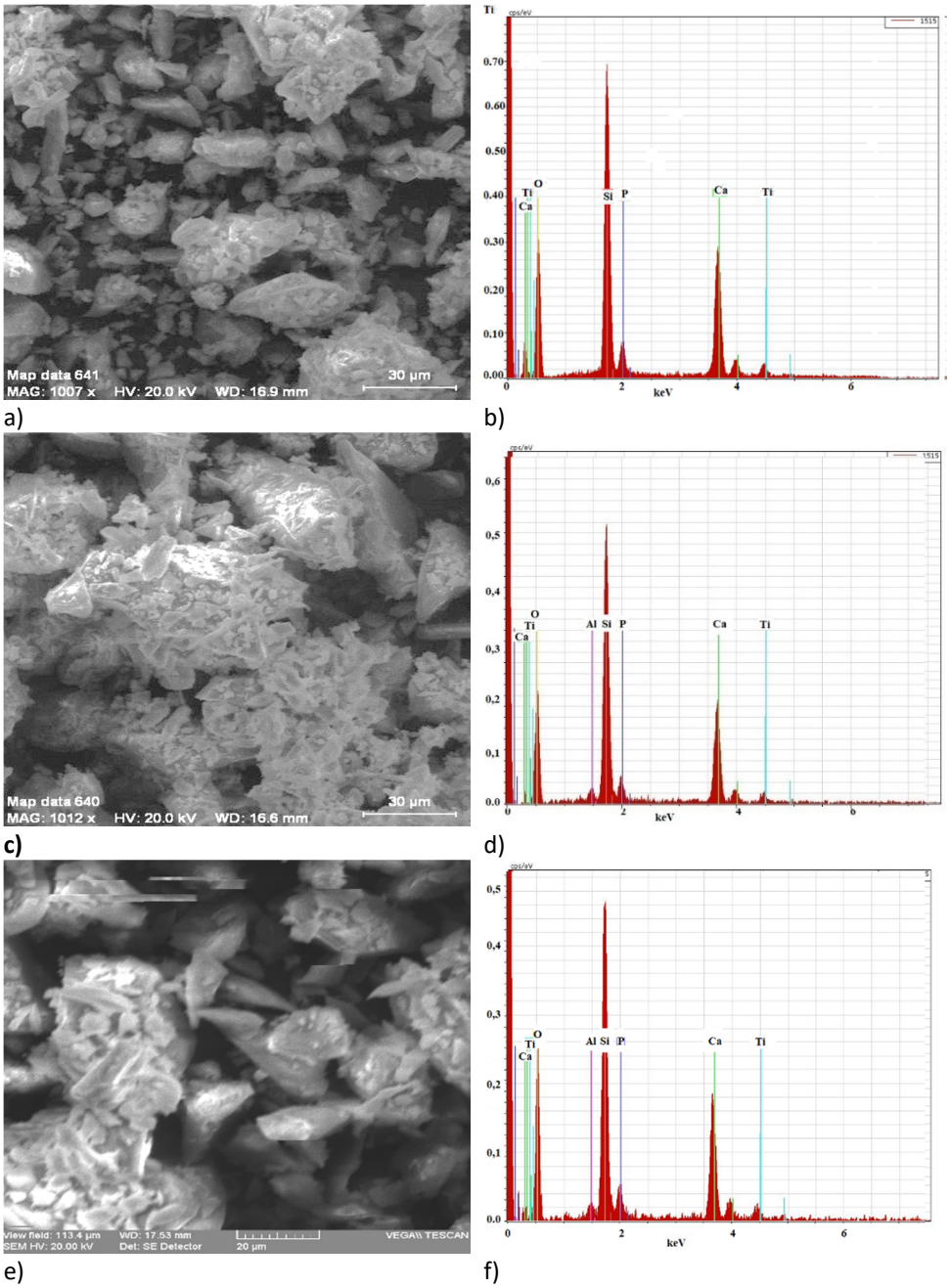

Fig.2. *SEM images and corresponding EDX spectra for the studied samples: a) and b) P_0; c) and d) sample P_1; e) and f) sample P_2.*

Table 2. Elemental composition (at %) and Ca/P ratio obtained by EDX analysis of sol-gel derived (66-x)SiO_2·27CaO·4P_2O_5·3TiO_2·xAl_2O_3 samples

Sample	Si	Ca	P	Ti	O	Al	Ca/P
P_0	18,82	8,23	2,42	0,90	69,80	-	3,26
P_1	23,12	5,83	2,86	0,55	66,40	1,24	2,03
P_2	19,13	7,54	2,58	1,02	68,50	1,12	2,63

The decrease in the Ca/P could be related to the increase in the phase reach in P_2O_5, favored, close to the hydroxyapatite reported for the bone tissue, by the aluminum oxide addition [21].

CONCLUSIONS

Samples of (66-x) SiO_2·27CaO·4P_2O_5·3TiO_2·xAl_2O_3 system (x = 0, 1 and 2 mol %) were prepared following the sol-gel route. Their structure was stabilized by 600 °C treatment. The XRD analysis points out that all samples are non-crystalline, regardless of Al_2O_3 addition. The SEM images show porous particles shaped as plated and whiskers, with sizes between 1-500 μm. The acicular form is prevalent for the composition with x = 1 mol % Al_2O_3. The elemental composition delivered by EDX analysis indicates for Ca/P ratio a close value to that of the nominal composition only for the sample without Al_2O_3, and diminished values of Ca/P ratio in Al_2O_3 containing samples. The Ca/P ratios obtained after Al_2O_3 addition on account of SiO_2 are closer to that of natural hydroxyapatite reported for bone tissue, that is an attractive property for biomedical applications in orthopedics and dentistry.

REFERENCES

1. D. Ksouri, H. Khireddine, A. Aksas, T. Valente, F. Bir, N. Slimani, B. Cabal, R. Torrecillas, J. D. Santos, *NovaBiotechnol Chim* 17(2), 150(2018).
2. R. A. Jalil, K. A. Matori, M. H. M. Zaid, N. Zainuddin, M. Z. A. Khiri, N. A. A. Rahman, W. N. W. Jusoh, E. Kul, *J. Spetrosc.(Hindawi)* 9170412 (2020).
3. N. Kourkoumelis, I. Balatsoukas, M. Tzaphlidou, *J Biol Phys*., 38(2), 279 (2012).
4. H. Zhang, B.W. Darvell, *Acta Biomaterialia*, 6 (8), 3216 (2010).
5. T. Kokubo, H. Takadama, *Biomater.,* 27, 2907 (2006).
6. D. Bellucci, A.Sola, R. Salvatori, A. Anesi, L. Chiarini, V. Cannillo, *Mater. Sci. Eng. C*, 43, 573 (2014).

7. D. Bellucci, A. Sola, M. Gazzarri, F. Chiellini, V. A. Cannillo, *Mater. Sci. Eng. C*, 33, 1091 (2013).
8. K. Magyari, R. Stefan, D.C. Vodnar, A. Vulpoi, L. Baia, *J. Non-Crystal. Solids* 402, 182 (2014).
9. K. Magyari, R. One, I.-S. Todor, M. Baia, V. Simon, S. Simon, L. Baia, *J. Raman Spectrosc.* 47, 1102 (2016).
10. M. Tamasan, H. Szilagyi, E. Vanea, V. Simon, *J. Optoelectron. Adv. M*. 15, 879 (2013).
11. J. R. Jones, *Acta Biomater.* 9, 4457 (2013).
12. E.A. Abou Neel, D.M. Pickup, S.P. Valappil, R.J. Newport, J.C. Knowles, *J. Mater. Chem*., 19, 690 (2009).
13. L.L. Hench, J.M. Polak, *Science*, 295, 1014(2002).
14. L. L. Hench, *J. Am. Ceram. Soc.,* 74, 1487 (1991).
15. T. Kokubo, *Biomaterials*; 12, 155 (1991).
16. Carta D, Knowles JC, Smith ME, Newport RJ, *J Non-Cryst Solids*, 353, 1141 (2007).
17. P. Kiran, V. Ramakrishna, M. Trebbin, N.K. Udayashankar, H.D. Shashikala, *J. Adv. Res.*, 8, 279 (2017).
18. M. Taherian, R. Roaeeb, M. Fathi, M. Tamizifar, *J. Adv. Ceram.* 3(3), 207 (2014).
19. D. Ksouri, H. Khireddine, A. Aksas, T. Valente, F. Bir, N. Slimani, B. Cabal, R. Torrecillas, J. D. Santos, *Nova Biotechnol Chim* 17(2), 150 (2018).
20. L. Baia, M. Baia, W. Kiefer, J. Popp, S. Simon, *Chem. Phys.,* 327, 63 (2006).
21. O. Kaygili, Tatar, Y. S. Keser, *J. Sol-Gel Sci. Technol.* 65,105 (2013).