Properties of calcium-phosphate materials obtained by sol-gel method: effect of MgO concentration

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Abstract. A calcium-phosphate system was obtained by sol-gel method from 0.4 M solutions based on ethyl alcohol, tetraethoxysilane, phosphoric acid, calcium nitrate, and magnesium nitrate. Two compositions with different content of CaO and MgO were prepared. After the maturation of solutions they followed by heat treatment at 60°C for 30 minutes and at 600°C and 800°C for 1 h. Solution with 20 wt.% MgO is suitable for film production up to seven days, while 5 wt.% MgO is available for creation of films only on the second day of its preparation. Thin films were obtained on the second day by spin-coating with a centrifuge speed of 3000 rev/min, followed by heat treatment at 60°C for 20 minutes and at 800°C for 1 h. The formation of crystalline phases in synthesized materials occurs at 800°C. An increase in the content of magnesium oxide in the system helps to accelerate the growth of particles on the surface of the samples when immersed in a simulation body fluid.

1. Introduction

Biomaterial is non-viable material intended for interaction with living tissue and performing medical functions. Three primary classes of biomaterials are mainly used as implants: metals, ceramics, and polymers. Calcium phosphate materials are of the greatest practical interest due to their high biocompatibility [1-4]. Due to good bioactivity, osteoconductivity, and biodegradability, calcium-phosphate materials are used as bone repair materials of fillers since they form a bond to living bone for more than ten years.

The most suitable method for calcium-phosphate materials preparation is sol-gel synthesis since it allows obtaining materials with different properties: fine crystalline and coarse-grained materials by changing initial reagents technological conditions [5-7].

Glass ceramics based on the SiO₂·P₂O₅·CaO system possess high bioactivity [8] depending on magnesium oxide additives. The relevance of magnesium for biomedical research is related to its fundamental role in cellular processes and human metabolism [9]. It is known that Mg stimulates the proliferation of osteoblasts and the ability of bone mineralization. Several studies have shown that divalent cations (Mg²⁺) play a key role in bone remodeling and skeletal development [10, 11]. Deficiency of Mg can be associated with a decrease in osteoclastic and osteoblastic activity, which leads to bone fragility and bone growth.
2. Experimental part
To obtain thin-film and dispersed materials based on the SiO$_2$-P$_2$O$_5$-CaO-MgO system, a film-forming solution was prepared. Ethyl alcohol of 96 wt.% was used as a solvent, and calcium nitrate and magnesium nitrate were added with occasional stirring until complete dissolution of the salts. Then phosphoric acid and tetraethoxysilane were added to the solution, with a total concentration of each substance 0.4 M.

For the preparation of solutions based on the SiO$_2$-P$_2$O$_5$-CaO-MgO system 2 compositions with different content of CaO and MgO were chosen (table 1).

| Oxide   | Composition Mg5 | Composition Mg20 |
|---------|-----------------|------------------|
| SiO$_2$ | 58              | 58               |
| P$_2$O$_5$ | 12            | 12               |
| CaO     | 25              | 10               |
| MgO     | 5               | 20               |

After ripening of the film-forming solution, thin-film and dispersed materials were obtained. Thin-film materials were obtained by centrifuging on an MPW-340 centrifuge at a speed of 3000 rpm on silicon substrates (as a reference), then a step heat treatment was carried out until the formation of a thin film. Drying was carried out at 60°C for 40 minutes followed by linear heating to 800°C. The samples were kept at 800°C for 1 hour prior to gradual cooling in the conditions of natural cooling of a muffle furnace. Dispersed materials obtained by drying the solutions at 60°C, followed by linear heating to 800°C.

The kinematic viscosity of the solutions was determined in a HPLC-2 capillary viscometer. The thermo-gravimetric analysis was performed on a NETSCH Jupiter STA 449 F1 thermal analyzer in the temperature range from 25 to 1000°C with a heating rate 30°/min in air atmosphere. The control of the evolved gas phase decomposition products was carried out with a NETZSCH QMS 403 D Aëolos mass spectrometer. IR spectra of dried solutions were reordered on a Agilent Cary 630 FTIR IR spectrometer in the frequency range of 400…4000 cm$^{-1}$. Phase composition of the dispersed materials was determined by X-ray diffraction on Rigaku MiniFlex 600 diffractometer (CuK$_\alpha$ radiation). Surface morphology of the obtained materials was studied using a scanning electron microscope (SEM) HITACHI TM-3000. Elemental composition was determined by X-ray microanalysis by using a Quantax-70 instrument. The thickness of the films was measured on a laser ellipsometer Sentech SE400adv. The measurements were carried out at three points along the entire surface of the film. Evaluation of the bioactivity of the obtained materials was studied using a cell-free simulation of the body fluid (SBF) for 14 days. Samples were placed in SBF at a 37 ± 0.5°C and pH = 7.4. The solution was changed every day for 14 days. The composition of the SBF solution is described in [12].

3. Results and discussion
Investigation of physicochemical processes occurring in solutions after their preparation was carried out by measuring the viscosity. On the first day, the viscosity of solutions has a value in the range from 1.77 to 1.82 mm$^2$/s depending on solution composition (table 2). On the second day, a significant decrease in viscosity value was observed in solution Mg5, and on the third day a white finely dispersed precipitation was precipitated. The Mg20 solution is stable for 13 days. At 14$^{th}$ day, a precipitate forms in the Mg20 solution. Thus, with increasing magnesium content in the system, the stability of solutions increases.

Precipitation in 5 wt.% MgO solution is caused by hydrolysis and polycondensation processes [13, 14] and electrostatic interaction between dissolved ions and solvent molecules, which can lead to both an increase and a decrease in the viscosity value. Since the viscosity of film-forming solutions
Valence vibrations of NO<sub>3</sub>- group, stretching vibrations of -CH<sub>2</sub>- and -CH<sub>3</sub> groups, deformation oscillations -OH in primary alcohols, stretching vibrations P=O, PO<sub>4</sub><sup>3-</sup> group, stretching vibrations of Si-O-Si, deformation oscillations of Si-O, deformation oscillations of Ca-O are present in solutions (table 3, figure 1). Further, despite different composition of solutions (table 3, figure 1 a, 1b) it can be seen that the peaks within the 3317...3326 cm<sup>-1</sup> range correspond to vibrations of free groups -OH. Within the range of 2870...2925 cm<sup>-1</sup> valence vibrations of -CH<sub>3</sub> and -CH<sub>2</sub>- are registered. Valence vibrations of P=O, -PO<sub>4</sub><sup>3-</sup> groups correspond to 1041...1045, 1088 cm<sup>-1</sup> (table 3).

Table 2. Viscosity values for prepared solutions in dependence on time, mm<sup>2</sup>/s.

| Solution | Storage time, day |
|----------|-------------------|
|          | 1  | 2  | 5  | 7  | 13 |
| Mg5      | 1.77 | 1.71 | 1.75 | 1.75 | 1.78 |
| Mg20     | 1.82 | 1.81 | 1.75 | 1.75 | 1.78 |

Regardless of the solution composition (figure 1 a, 1b) deformational oscillations of H<sub>2</sub>O are observed. Besides, vibrations of NO<sub>3</sub>-group, stretching vibrations of -CH<sub>2</sub>- and -CH<sub>3</sub> groups, deformation oscillations -OH in primary alcohols, stretching vibrations P=O, PO<sub>4</sub><sup>3-</sup> group, stretching vibrations of Si-O-Si, deformation oscillations of Si-O, deformation oscillations of Ca-O are present in solutions (table 3, figure 1). Further, despite different composition of solutions (table 3, figure 1 a, 1b) it can be seen that the peaks within the 3317...3326 cm<sup>-1</sup> range correspond to vibrations of free groups -OH. Within the range of 2870...2925 cm<sup>-1</sup> valence vibrations of -CH<sub>3</sub> and -CH<sub>2</sub>- are registered. Valence vibrations of P=O, -PO<sub>4</sub><sup>3-</sup> groups correspond to 1041...1045, 1088 cm<sup>-1</sup> (table 3).

Table 3. IR spectrometry results for solutions.

| Mg5 Frequency, cm<sup>-1</sup> | Mg20 Frequency, cm<sup>-1</sup> | Vibrational modes                                |
|-----------------------------|---------------------------------|--------------------------------------------------|
| 3324                        | 3322                            | Free -OH groups                                  |
| 2974; 2879                  | 2974; 2875                      | Stretching vibrations of -CH<sub>3</sub> groups   |
| 2925                        | 2927                            | Stretching vibrations of -CH<sub>2</sub>- groups  |
| 1653                        | 1649                            | Deformation oscillations H<sub>2</sub>O           |
| 1442; 1408; 1380            | 1453; 1418; 1373                | Bending mode of NO<sub>3</sub>- group            |
| 1317                        | 1328                            | Deformation oscillations -CH<sub>3</sub>-        |
| 1269                        | 1274                            | Deformation oscillations -OH in primary alcohols |
| 1088; 1045                  | 1088; 1041                      | Stretching vibrations of P=O, -PO<sub>4</sub><sup>3-</sup> groups |
| 801                         | 795                             | Stretching vibrations of Si-O-Si                 |
| 879                         | 877                             | Stretching vibrations of Si-O-H                  |
| 605                         | 601                             | Deformation oscillations of Si-O-                |
| 426                         | 436                             | Deformation oscillations of Ca-O-                |

Within the range of 795 – 801 cm<sup>-1</sup> valence vibrations of Si-O-Si are registered and in the section of 877 – 879 cm<sup>-1</sup> valence vibrations of Si-O-H are registered. The presence of these bonds indicates the formation of the molecular framework, which, according to the literature [7, 12], is formed as a result of hydrolysis and polycondensation of tetraethoxysilane.

The thermal analysis of dried solutions and the X-ray phase analysis of the products of their thermal destruction have allowed us to establish the formation processes of the samples as optimal temperature of synthesis (figure 2) and the composition of substances formed during the thermolysis of dried solutions (figures 5 and 6). The process of the material forming occurs in three stages (figure 2). The first stage is at the temperature from 50°C to 200°C. It is corresponding to an endothermic effect in the DSC curve at 104°C. It is due to the removal of physically and chemically bounded water and it is accompanied by a large mass loss. The second stage (with less weight loss) is commenced after the end of the first stage (at 200°C) and run on until 600°C. It is corresponding to an exothermic peak at 230°C. It is probably related with the loss of nitrates and organics (i.e. alkoxy group). The...
third stage (without changing the mass) is began after 600°C. It is corresponding to an endothermic effect in the DSC curve at 800°C. It is associated with the transition of amorphous structures to crystalline.

![Figure 1. IR spectrometry results for solutions (a) Mg5, (b) Mg20.](image)

![Figure 2. Thermal analysis data for the composition Mg20.](image)
Figure 3. IR spectrometry results for dispersed materials annealed at 600°C (a) Mg5, (b) Mg20.

Figure 4. IR spectrometry results for dispersed materials annealed at 800°C (a) Mg5, (b) Mg20.

The frequencies 715, 790 - 803 cm\(^{-1}\) correspond to the oscillations of the chains of siloxanes \(\delta (\text{Si-O-Si})\) (figure 3). The Si-O-Si bond vibrations indicate the formation of a molecular framework as a result of hydrolysis and polycondensation of tetraethoxyxilane [15, 16]. With an increase in the temperature treatment to 800°C, the oscillations of 438 - 456 cm\(^{-1}\) are attributed to deformation Ca-O-vibrations (figure 4.), which indicates the incorporation of calcium ions into the molecular framework with the formation of crystalline products and is consistent with the results of X-ray phase analysis.

X-ray diffraction data show that annealed at 600°C powders are amorphous. In sample Mg5 quartz SiO\(_2\) and vitlokite Ca\(_{2.589}\)Mg\(_{0.411}\)(PO\(_4\))\(_2\) were identified (figure 5). In sample Mg20, \(\beta\)-cristobalite SiO\(_2\) and stentifeldite Mg\(_3\)Ca\(_3\)(PO\(_4\))\(_4\) were detected (figures 6).

Figure 5. XRD patterns of sample Mg5 annealed at 800°C (*) SiO\(_2\), (#) Ca\(_{2.589}\)Mg\(_{0.411}\)(PO\(_4\))\(_2\)

Figure 6. XRD patterns of sample Mg20 annealed at 800°C (*) SiO\(_2\), (#) Mg\(_3\)Ca\(_3\)(PO\(_4\))\(_4\)

According to ellipsometry data, increase of MgO content in the system leads to the decrease of films’ thickness (table 4).

| Sample | Thickness, nm |
|--------|--------------|
| Mg5    | 34.68±0.5    |
| Mg20   | 43.91±0.5    |

Table 4. Thickness of films obtained on silicon substrates

To study the bioactive properties, the samples were immersed in a solution of SBF for 14 days.
Figure 7. SEM images of films with a MgO content of 5 wt.% before (a) and after soaking in SBF for 3 (b), 7 (c) and 14 days (d).

Figure 8. SEM images of films with a MgO content of 20 wt.% before (a) and after soaking in SBF for 3 (b), 7 (c) and 14 days (d).
The study of the morphology of the coatings obtained after immersion in the SBF solution using electron scanning microscopy revealed large loose particles on the surface. Spherical particles with a size of 1.9-3.6 nm are fixed on the surface after holding the samples for 3 days (figure 7b, 8b). With an increase in storage time up to 7 days, the growth of needle particles in the surface is fixed (figure 7c, 7d). At 14 days holding samples in solution, the particles continue to grow and increase in size and reach 17.8–30 nm (figure 7d, 8d). The presence of needle particles contributes to the formation of a network structure on the surface of the samples, which is favorable for the further in growth of bone tissue in them and the formation of a stronger implant-bone connection. Increasing the magnesium content in the system helps to accelerate the growth of particles on the surface of the samples.

4. Conclusion
Glass ceramics based on SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-CaO system possess high bioactivity [8] depending on the addition of magnesium oxide. Thus we synthesized dispersed materials and thin films based on the system SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-CaO-MgO by sol-gel method. For the preparation of solutions based on the SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-CaO-MgO system 2 compositions with different content of calcium and magnesium were chosen. Solution with MgO content of 20wt.% is suitable for film production up to 7 days (thickness of films obtained on silicon substrates 43.9±0.5). Solution with a magnesium content of 5 weight percent is available for creation of films only on the second day of its preparation (thickness of films obtained on silicon substrates 34.68±0.5). The formation of crystalline phases in synthesized materials occurs at 800°C. In sample Mg5 quartz SiO<sub>2</sub> and vitlokite Ca<sub>2</sub>SiO<sub>3</sub>MgO<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were identified. In sample Mg20, β-cristobalite SiO<sub>2</sub> and stentifieldite Mg<sub>6</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> were detected. Increasing MgO content in the system helps to accelerate the growth of particles on the surface of the samples when immersed in a solution of SBF, thereby increasing the bioactivity materials.

Acknowledgments
The results were obtained within the framework of the state task of the Ministry of Education and Science of the Russian Federation, project No.10.2281.2017/4.6.

References
[1] Barinov S M 2010 Calcium phosphate-based ceramic and composite materials for medicine Russ. Chem. Rev. 79 13
[2] Komlev V S, Rau J V, Fosca M, Fomin A S, Gurin A N, Barinov S M and Caminiti R 2012 Single-phase bone cement based on dicalcium phosphate dihydrate powder and sodium silicate solution Materials Lett. 73 115
[3] Barinov S M and Komlev V S 2016 Approaches to the fabrication of calcium phosphate-based porous materials for bone tissue regeneration Inorg. Mater. 52,4 339
[4] Lytkina D, Berezovskaya A, Korotchenko N, Kurzina I and Kozik V 2017 Preparation of composite materials based on hydroxyapatite and lactide and glycolide copolymer AIP Conf. Proc. 1899 020011514
[5] Jamal N and Bouaziz J 2017 Synthesis, characterization and bioactivity of a calcium-phosphate glass-ceramics obtained by the sol-gel processing method Mat. Sci. Eng. 71 279
[6] Petrovskaya T, Borilo L and Kozik V 2016 The processes in film-forming solution based on tetraethoxysilane, phosphoric acid and calcium chloride AIP Conf. Proc., 1771 0200061
[7] Kukueva E V, Putlyaev V I, Tikhonov A A and Safronova T V 2017 Octacalcium phosphate as a precursor for the fabrication of composite bio ceramics Inorg. Mater. 53,2 212
[8] Borilo L P, Lyutova E S and Spivakova L N 2016 Study of biological properties of thin-film materials on the basis of the SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-CaO system Key Eng. Mater. 683 427
[9] Moghanian A, Sedghi A, Ghorbanoghi A and Salari E 2018 The effect of magnesium content on in vitro bioactivity, biological behavior and antibacterial activity of sol–gel derived 58S bioactive glass Ceramics Int. 44 9422
[10] Chubanov V, Mittermeier L and Gudermann T 2018 Role of kinase-coupled TRP channels in
mineral homeostasis *Pharmacol. Therapeut.* **184** 159

[11] Nabiyouni M, Brückner T, Zhou H, Gbureck U and Bhadur S B 2018 Magnesium-based bioceramics in orthopedic applications *Acta Biomaterialia*, vol 66 pp 23-43

[12] Kokubo T, Kushitani H and Sakka S 1990 Solutions able to reproduce in vivo surface – structure changes in bioactive glass – ceramic *Biomaterials* **24** 721

[13] Borilo L P and Lyutova E S 2017 Synthesis and properties of bioactive thin-film materials based on the SiO$_2$–P$_2$O$_5$–CaO and SiO$_2$–P$_2$O$_5$–CaO–TiO$_2$ systems *Inorg. Maters.* **53** p 400

[14] Suykovskaya NV 1971 Chemical methods for the synthesis of thin films (Leningrad: Chemistry) p 230

[15] Zhang D, Wang M, Ren GJ and Song EJ 2013 General relation between tensile strength and fatigue strength of metallic materials *J. Mater. Sci. Eng.* **33** 4677

[16] Letaef N, Lucas-Girot A, Oudadesse H, Dorbez-Sridi R and Boullay P 2104 Investigation of the surfactant type effect on characteristics and bioactivity of new mesoporous bioactive glass in the ternary system SiO$_2$–CaO–P$_2$O$_5$: Structural, textural and reactivity studies *Acta Biomaterialia* **195** 109