ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 789−793. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.A. Sinyaev, L.V. Levchenko, E.S. Shustikova, R.A. Karzhaubaeva, G.D. Gaysina, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 5, pp. 737−741.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Precipitated Calcium Phosphatesilicates and Their Dehydration in Air at Room Temperature

V. A. Sinyaev, L. V. Levchenko, E. S. Shustikova, R. A. Karzhaubaeva, and G. D. Gaysina

Bekturov Institute of Chemical Sciences of the Ministry of Education and Science of Republic Kazakhstan, Alma Ata, Kazakhstan

Received June 9, 2008

Abstract—By exchange reaction in the aqueous solutions between sodium phosphatesilicates and calcium chloride is obtained a group of the crystalline and amorphous substances, which contain up to 80 wt % of water. Dehydration of amorphous calcium phosphatesilicates at room temperature is studied.

DOI: 10.1134/S1070427209050073

The high biocompatibility of synthetic calcium phosphates is a reason for their use in stomatology, orthopedics and surgery for replacing the sick or lost bone tissue [1–6]. Among calcium phosphates are significant the amorphous ones, which are of high independent value for medicine [4, 7–13]. Because of the increased chemical activity and the dispersiveness of components at the level close to the molecular, they are also of interest as the precursors of calcium phosphate ceramics [14–16]. Usually the amorphous phosphates are obtained from the solution, by precipitating them in the presence of the inhibitors of apatite crystallization, for example diphosphate, carbonate and fluoride salts of magnesium [4, 7, 8, 17–19]. Other substances also are used, for example soluble silicates, which increasingly supplement phosphates in the composition of diverse phosphate biomaterials [20–23]. It was noted that silicates increase the biocompatibility of calcium phosphates [24]. Unfortunately, little known about the nature of amorphous calcium phosphate-silicates.

In this work is described obtaining of amorphous calcium phosphate-metasilicate from solution and are presented the data about its dehydration in air at room temperature.

EXPERIMENTAL

For the synthesis of amorphous calcium phosphate-metasilicate is used sodium hydrogen phosphate $Na_2HPO_4 \cdot 12H_2O$, sodium metasilicate $Na_2SiO_3 \cdot 9H_2O$ of "analytically pure" grade, and calcium chloride $CaCl_2 \cdot 6H_2O$ of "pharmacopoeial" grade.

The synthesis of calcium phosphate-silicates was carried out employing the procedure described earlier [25]. Aqueous 5% solutions of sodium hydrogen phosphate and metasilicate at vigorous stirring were mixed in the necessary proportions. Then the solution of calcium chloride was added dropwise. Preliminarily into the phosphate-silicate solution was added alkali (NaOH) in the amount sufficient for neutralization of the acid evolved in the course of the formation of calcium phosphates. Precipitation was ceased at reaching the value of pH 8. The aqueous suspensions of the precipitated substances were separated from the solutions of salts by decantation, dispersed in the distilled water with pH 8 taken approximately in the 10-fold excess, settled 2–3 h and again separated from the solution. Operation was repeated to the absence in the wash waters of ions Cl^-. The washed products were filtered in a vacuum on the nylon filter of "Corning" firm with porous size 0.2 μ. All operations were carried out at room temperature.

For investigating the synthesized substances were used the methods of the IR Fourier transform spectroscopy, thermal and X-ray phase analysis. IR spectra were registered on a FT-IR Nicollet 5700 spectrometer in the regimes of the disrupted total internal reflection (TIR) and the light transmission. In the first case the samples were applied by the layer with a thickness of 1 mm to the horizontal unit of the the single-crystal ZnSe, the spectra were taken with the resolution 4 cm^{-1}, the accuracy of the measurements is ±0.5 cm^{-1}, the number of scans 32. In the second case the substance dried at room temperature in air was dispersed in the medium of solid KBr and

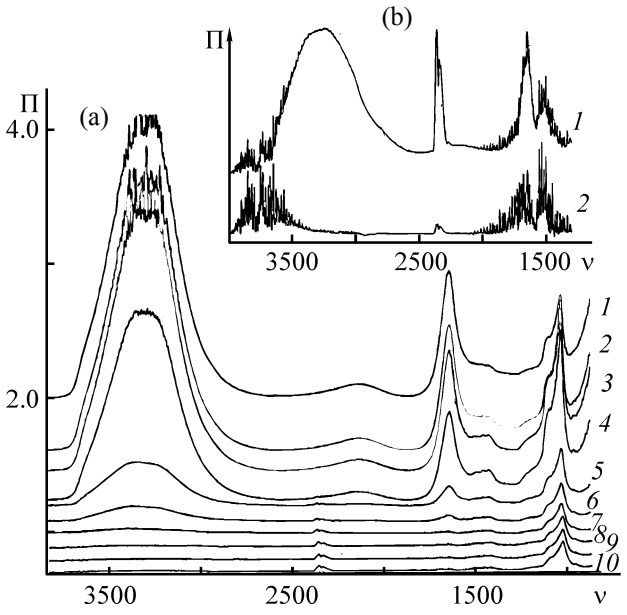

Fig. 1. Change in IR Fourier spectra of amorphous phosphate-silicate during maintaining it in air at room temperature for different periods τ (a), and IR Fourier spectra of (*1*) amorphous phosphatesilicate after 118 min of dehydration and (*2*) air saturated by gaseous water (b). Π is absorption (rel. un.), ν is wave number (cm^{-1}); the same for Fig. 3, 4. τ (min): (*1*) 0, (*2*) 34, (*3*) 54, (*4*) 59, (*5*) 64, (*6*) 69, (*7*) 74, (*8*) 79, (*9*) 84, (*10*) 118.

analyzed employing known procedure. The X-ray phase analysis was carried out on a DRON-3 diffractometer with the CoK_α-emission. For the thermal analysis was used termoanalizer Mettler Toledo TGA/SDTA 851, measurement were conducted in the open corundum crucibles with the weighted quantity of substance of approximately 100 mg at constant temperature 25°C.

As a result of the exchange reactions in the solutions between phosphate, silicate and their binary mixtures, on one hand, and calcium chloride on the other hand, are formed the pastelike strongly hydrated products. In Fig. 1a as an example is given the IR TIR spectrum of calcium phosphate, precipitated in the presence of 60 mol % of metasilicate. It is seen that in the high-frequency region there is a powerful line ν(OH) of water molecules, and in the range 1600–1700 cm^{-1} less strong band, related to the corresponding deformation vibrations δ(OH) [25–28]. Besides, in the long-wave region of the spectrum there is an absorption caused by the vibrations of the chemical bonds P–O and Si–O [18, 29–34]. In air in time the lines belonging to the molecules of water in the spectrum weaken, and the bands related to the bonds P–O and Si–O, although decrease in intensity, but substantially slower, and as a result they become prevailing (Fig. 1). Earlier has already been noted that the similar redistribution of the intensity of the spectral bands related to the vibrations of the bonds O–H and P–O occurs in the IR spectra of other amorphous calcium phosphates [32]. Reason for this is increase in the concentration of inorganic substance caused by the removal of moisture.

Analogous results are obtained for other precipitated calcium phosphate-silicates: at room temperature in air they all lose major part of the connected moisture, retaining nevertheless about 20% of the initial amount.

It is noticeable that the profiles of the bands in the IR spectra of the bonds P–O and Si–O are practically identical in the spectra of the initial hydrated substances and the products of their dehydration. This points to the fact that in the course of drying the salt part of the precipitated materials in essence preserves its phase nature. The data about the phase composition of dehydration products completely can be extended over the strictly precipitated substances. The results of spectroscopic study of dehydration products are given below.

The substance, precipitated by calcium chloride from the solution of sodium hydrogen phosphate and kept at room temperature in air to constant mass is

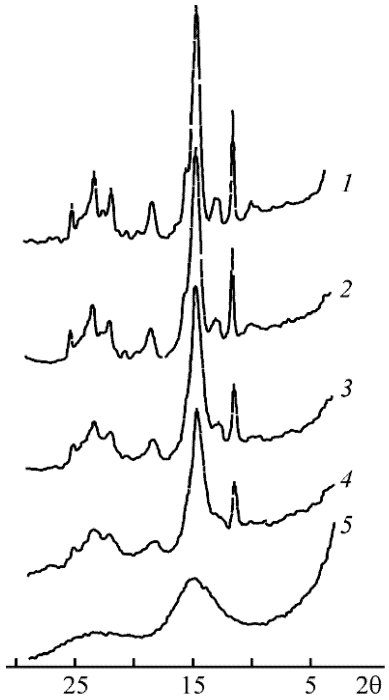

Fig. 2. Diffractograms of the substances, precipitated by calcium chloride from the aqueous phosphate-silicate solutions. 2θ is Bragg angle (deg). Content of silicate (mol %): (*1*) 0, (*2*) 10–20, (*3*) 30, (*4*) 40–50, (*5*) 60.

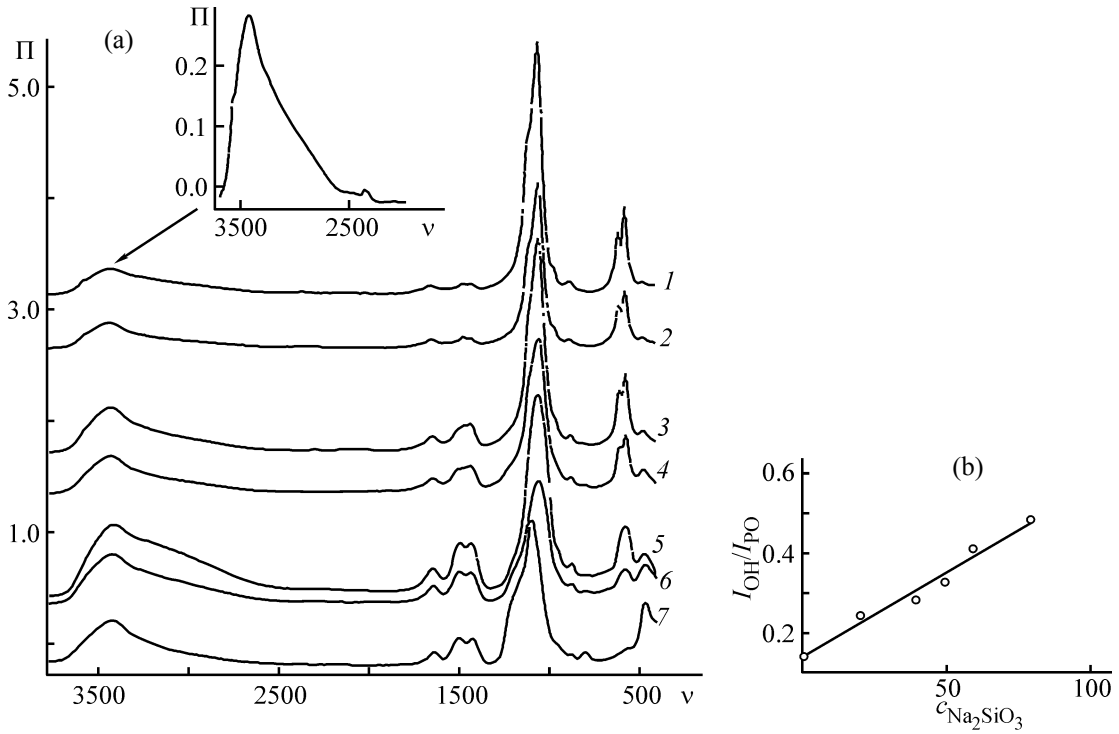

Fig. 3. IR spectra of the substances, precipitated by calcium chloride from the aqueous phosphatesilicate solutions (a), and change in the relative intensity of bands ν (OH) and ν (PO) in the spectra depending on the content of silicate $c_{Na_2SiO_3}$ (mol %) in the parent solutions (b). Content of silicate (mol %): (*1*) 0, (*2*) 20, (*3*) 40, (*4*) 50, (*5*) 60, (*6*) 80, (*7*) 100.

hydroxoappatite, since in its diffractogram occur the reflexes characteristic of crystalline $Ca_5(PO_4)_3OH$ (Fig. 2). The apatite attributes are less distinct in the product formed in the presence of 10–20 mol % of sodium metasilicate. With an increase in the concentration of the latter to 50 mol % are formed the products with ever more weakened features of crystalline salts. At the content of silicate of approximately 60 mol % the product acquire the nature of the amorphous substance, on diffractogram of which there are only two very wide maximums. The substances even richer in silicate again loss the amorphous nature, since at the appropriate diffractograms again appear the reflexes related to the crystalline components.

The analysis of air-dry materials by the method of IR spectroscopy in the regime of absorption confirmed that from the solution of sodium hydrogen phosphate is obtained hydroxoapatite (Fig. 3a). Actually, the set of lines in the region of 500–1500 cm^{-1} of the spectrum of this substance completely corresponds to the spectra of apatites described in the literature [18, 29, 30]. In accordance with the nature of lines in the region of the stretching vibrations of chemical bonds P–O (950–1200 cm^{-1}), hydroxoapatite is not a completely crystalline substance, since the corresponding maximums are weakly resolved and broad. The bands corresponding to the deformation and stretching vibrations of OH bonds OH in water molecules indicate the presence in the dehydration products of residual moisture. At the band of ν(OH) from the high-frequency side is seen a relatively weak peak at a frequency about 3560 cm^{-1}, which usually is assigned to the vibrations of OH bonds in the discrete hydroxyl groups of the apatite $Ca_5(PO_4)_3(OH)$ [18, 30]. Furthermore, in the ranges of 1400–1600 and 870–880 cm^{-1} there are the bands which testify about the presence in the product of the admixture of carbonate [18], probably co-precipitated in the course of the synthesis.

The IR spectrum of the product obtained by the precipitation of calcium phosphate in the presence of 20 mol % of sodium silicate differs little from the previous spectrum, especially in the low-frequency region. However, at the opposite end of the spectrum the difference is more noticeable. In particular, the line corresponding to the vibrations of bonds OH in discrete hydroxides becomes weak and blur. Even more explicit changes are noticeable in the spectrum of the substance synthesized in the presence of 40 mol % of silicate, where the second in the intensity line, which lies in the region of the stretching vibrations of P–O bonds, and the

band of discrete hydroxyl are converted into the badly distinguishable shoulders.

Further increase in the content of silicate in the substance to 50 mol % leads to broadening of the line belonging to stretching vibrations ν(PO), and high-frequency shoulder on it becomes even less distinct. The spectrum of calcium phosphate containing about 60 mol % of silicate acquires the features inherent in amorphous substances. This is indicated by the band in the region of 950–1200 cm^{-1}, which is transformed into a broad maximum, and by lines in the regions of 500–650 cm^{-1} merging into one broad band. In the spectrum of next product the line, which corresponds to ν(PO) by its nature approximately the same, but additionally on it appears a high-frequency shoulder, which in the spectrum of precipitated calcium silicate becomes the strongest one. According to the data of [31, 33, 34] this line corresponds to the stretching vibrations of Si–O bonds in the silicate gels. Other, weaker peaks in the last spectrum correspond to deformation vibrations δ(Si–O) in the SiO_4 tetrahedrons (range 400–500 cm^{-1}) and to vibrations of C–O bonds in the anions CO_3^{2-} (ranges 1400–1600 and 870–880 cm^{-1}). Note that in the spectrum of this sample, as in previous spectra, is not seen the line with the maximum at approximately 650 cm^{-1}, which corresponds to the stretching vibrations of bridgehead bonds Si–O–Si.

The analysis of the structure of the strongest spectral band in the region 950–1250 cm^{-1} after the application of a method of Fourier transform showed that in the substances containing up to 50 mol % of silicate this line consists of two components (Fig. 4). The IR spectrum of the most amorphous product contains only one broad component. However, absorption of calcium silicate again is split into two peaks, which, however, differ from those in the spectra *1–4* (Fig. 4). Obviously, upon enrichment of the precipitated products by silicate up to 50 mol % occurs a smooth, but not cardinal change in the structure of substances with the retention of order and interatomic organization more inherent in hydroxoapatites. Everything is changes at the content of silicate approximately 60 mol %: appear the chemical bonds P–O and Si–O, which by the parameters differ from the bonds P–O in calcium phosphate and from the bonds Si–O in silicate, which is inherent in amorphous state.

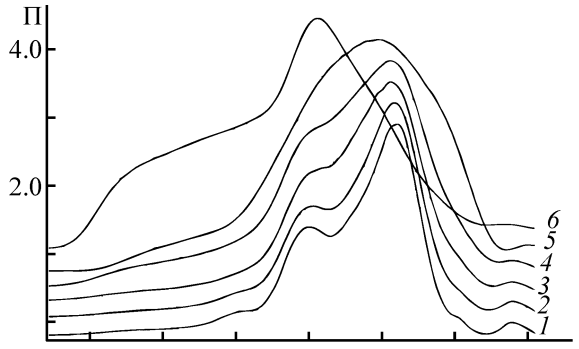

Fig. 4. Structure of absorption bands in the region of stretching vibrations of the bonds P–O and Si–O in the IR spectra of the substances, precipitated by calcium chloride from the phosphate-silicate solutions. Content of silicate (mol %): (*1*) 0, (*2*) 20, (*3*) 40, (*4*) 50, (*5*) 60, (*6*) 100.

It should be noted that an unexpectedly large quantity of silicate is required for the formation of crystalline apatite, about 60 mol %, while for achievement analogous aim at the use of diphosphate is needed almost a half amount of the inhibitor [25, 35]. Nevertheless from Fig. 4 it is evident that the presence in the composition of the precipitated product even of a small quantity of silicate affects the state of the P–O chemical bonds: the energy, necessary for the excitation of such bonds, rises with an increase in the content of silicate in the substances.

Amorphous calcium phosphate–silicate is most interesting as the ceramic precursor. This substance was already described above. Here we note that at the dehydration in air it adsorbs gaseous carbon dioxide. This is distinctly seen in Fig. 1, where in the range 2340–2360 cm^{-1} appear the lines characteristic of the stretching vibrations of bonds C–O in the molecules of gaseous CO_2 [36]. Furthermore, dehydration products contain gaseous water. Let us note that evacuation leads to rapid disappearance of H_2O and CO_2 from dehydration products. All this gives grounds to assume that dehydration products are of high porosity. High porosity is generally inherent in the products of dehydration of precipitated calcium phosphates [16].

CONCLUSIONS

1. Crystalline and amorphous substances are formed during the joint co-precipitation of calcium phosphate and silicate. The latter are formed at the molar ratio phosphate: silicate ~ 0.4 : 0.6. From the solutions richer in phosphate or silicate are precipitated the products close by their structure to hydroxoapatite or the calcium-silicate gel. In some of them an admixture of carbonate is present.

2. The water content in the calcium phosphate-silicates reaches 80 wt %. Amorphous phosphate-silicate already at room temperature loses major part of the bound moisture, preserving amorphous nature. In this case it absorbs carbon dioxide from air.

3. Dehydration products contain also gaseous water, which is removed at the evacuation of product.

REFERENCES

1. Aoki, H., *Science and Medical Applications of Hydroxyapatite,* Tokyo: JAAS, 1991, 245 p.
2. LeGeros, R.Z. and LeGeros, J.P, *An Introduction to Bioceramic*, Hench, L.L. and Wilson, J., Eds., London: World Scientific, 1993, p. 139.
3. Brown, P.W. and Constants, B.*, Hydroxyapatite and Related Raterials*, Boca Raton FL: CRC Press, 1994.
4. *Heorganicheskie fosfatnye materialy* (Inorganic Phosphate Materials), Kanazava, T., Ed., Kiev: Naukova Dumka, 1998.
5. Hench, L.L, *J. Am. Ceram. Soc*., 1998, vol. 81, no. 7, pp. 1705–1728.
6. Orlovskii, V.P., Komlev, V.C., and Barinov, C.M, *Neorgan. Materialy*, 2002, vol. 38, no. 10, pp. 1159–1172.
7. US Patent 6024985, A61K6/033; A61L27/12; C01B25/32; A61F2/00; *Bone Materials*.
8. EU Patent 1787954, A61L27/00, C01B25/32; A61F2/28; *Bone Substitution Material and a Method of the Manufacture.*
9. Mexican Patent 05002379, A61K33/42; A61K33/42; *Process for Preparation a Calcium Phosphate– Based Biocompound.*
10. PST Patent 2006130913, MPK, A61K8/24; A61K8/20; A61K8/22; *Dental Mineralization*.
11. Japan Patent 2007001970A61K8/19; A61Q1/12; A61Q19/02; *Cosmetic*.
12. Japan Patent, 2007217319, A61K8/25; A61Q1/10; A61K8/19; A61Q1/02; Makeup Cosmetic.
13. Chine Patent 1935636, C01B25/32; C01B25/00; *Method for Preparing Nano Aamorphous Calcium Phosphate Powder.*
14. Sinyaev, V.A., Shustikova, E.C., Griggs, D., and Dorofeev, D.V., *Fizika i Khimiya Stekla*, 2005, vol. 31, no. 5, pp. 924–928.
15. Sinyaev, V.A., Griggs, Dzh., Levchenko, L.V. et al., Abstracts of Papers, *I Mezhdunar. nauch.-prakt. konf. "Sovremennye polimernye materialy v meditsine i meditsinskoi tekhnike,*" (1st Int. Sci. Pract. Conf. on Polymeric Materials in Medicine and Medical Engineering), SPb, 2005, pp. 34–38.
16. Sinyaev, V.A., Dorofeev, D.V., Shustikova, E.C. et al., Abstracts of Papers,*Vseros. soveshch. "Biokeramika v meditsine*," 2006; Moskva In-t Fiziko-khimicheskikh problem i keramicheskikh materialov, PAH, pp. 29–30.
17. Harper, R.A. and Posner, A.S., *Mat. Res. Bull*., 1970, vol. 5, nol. 2, pp. 129–136.
18. LeGeros, R.Z., Shirra, W.P., Miravite, M.A., and LeGeros, J.P.*, Coll. Int. CNRS*, no. 230: "Physico-chimie et Cristallographie des Apatites d'Intérèt Biologique," Paris, 1973, pp. 105–115.
19. LeGeros, R.Z.*, Tooth*, Enamel I.Y., Fearnhead R.W., and Suga S., Eds., Amsterdam: Elsevier Sci. Publishers, 1984, p. 32.
20. US Patent 6846493 A61L27/12; C04B35/447; C04B38/00; C23C30/00. *Synthetic Biomaterial Bompound of Balcium Phosphate Phases Particularly Adapted for Supporting Bone Bell Activity.*
21. Coin, A.V., Evdokimov, P.V., Veresov, A.G., and Putlyaev, V.I., *Al'ternativnaya Energetika i Ekologiya*, 2007, no. 1(45), pp. 130–132.
22. Song, H., Kim, S.R., Jang, S.J. et al., *Bioceramics*, 2005, vol. 17, pp. 169–172.
23. Botelho, C.M., Brooks, R.A., Kawai, T. et al., *Bioceramics*, 2005, vol. 17, pp. 461–464.
24. Thian, E.S., Huang, J., Best, S.M. et al.*, Bioceramics*, 2005, vol. 17, pp. 445–448.
25. Sinyaev, V.A., Levchenko, L.V., Shustikova, E.C., and Griggs, D.*, Zh. Prikl. Khim*., 2003, vol. 76, no. 4, pp. 529–532.
26. Yukhnevich, G.V.*, Uspekhi Khimii*, 1963, vol. 32, no. 11, pp. 1397–1423.
27. Millo, A., Raichlin, Y., and Katzir, A., *Appl. Spectroscopy*, 2005, vol. 59, no. 4, pp. 460–466.
28. Mutter, R., Mecke, R., and Luttke, W.*, Z. Phys. Chem. Neue Folge*, 1959, vol. 19, no. 1/2, pp. 83–88.
29. Plyler, E.K. and Acguista, N., *J. Opt. Soc. Am.,* 1954, vol. 44, nol. 6, pp. 505–511.
30. Stutman, J.M., Termine, J.D., and Posner, A.S.*, Transactions*, New York: Acad. Sci., 1965, Ser. II, vol. 27, no. 6, pp. 669–675.
31. Marconic, M., Fowler, B.O., and Tung, M.S.*, J. Res. Natl. Inst. Stand. Technol*., 2004, vol. 109, no. 6, pp. 553–568.
32. Sinyaev, V.A., LeGeros, P.Z., Levchenko, L.V. et al., *Zh. Obshch. Khim*., 2008, vol. 78(140), no. 5, pp. 722–725.
33. Fujii, E., Kawabata, K., and Yoshimatsu, H. et al.*, J. Ceram. Soc. Japan*, 2003, vol. 111, no. 1298, pp. 762–766.
34. Saravanapavan, P. and Hench, L., *J. Non-Cryst. Solids*, 2003, vol. 318, nos. 1–2, pp. 1–13.
35. Fernandez, L., Alonso, C., Hidalgo, A., and Andrade, C.*, Advances in Cement Research*, 2005, vol. 17, no. 1, pp. 9–21.
36. Barinov, S.M. and Komlev, V.S.*, Biokeramika na osnove fosfatov kal'tsiya* (Bioceramics on the Basis Calcium Phosphates), Moscow: Nauka, 2005, 203 p.