

Effect of fluorine addition on the structure and properties of high-porous glass ceramics applicable for reconstructive surgery

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Effect of fluorine introduction into composition of high-porous glass ceramics based on biogenic hydroxyapatite and glass of the $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ system on structure and properties of the material obtained via doubling the polymer matrix structure has been studied. It is established that during sintering of samples from high-porous glass ceramics at 900°C a partial decomposition and/or interaction of hydroxyapatite with the glass phase occur, that results in forming the multiphase ceramics containing renanite, calcium silicophosphate, calcium pyrophosphate, pectolite and hydroxyapatite. In addition, in the case of fluorine introduction, fluorapatite is formed and sample strength increases by 30 % along with slight decrease in solubility *in vitro*.

Keywords: hydroxyapatite, fluorapatite, glass, high-porous biomaterial, implant.

Исследовано влияние добавки фтора, введённой в состав высокопористой стеклокерамики на основе биогенного гидроксиапатита и стекла системы $\text{SiO}_2\text{-CaO-Na}_2\text{O}$, на структуру и свойства материала, полученного методом дублирования структуры полимерной матрицы. Установлено, что при спекании образцов высокопористой стеклокерамики при 900°C происходит частичное разложение гидроксиапатита и/или его взаимодействие со стеклофазой, в результате чего образуется многофазная стеклокерамика, содержащая в своём составе ренанит, силикофосфат кальция, пирофосфат кальция, пектолит и гидроксиапатит, а при введении в состав образцов фтора образуется также фторапатит. Показано также, что введение фтора позволяет более чем на 30 % повысить прочность образцов, а также незначительно уменьшить растворимость *in vitro*.

Вплив добавки фтору на структуру та властивості високопористої стеклокераміки для реконструктивної хірургії. *О.Є.Сич, А.П.Яценко, Т.В.Томила, Г.Б.Товстоног, Я.І.Євич.*

Досліджено вплив добавки фтору, введеної до складу високопористої стеклокераміки на основі біогенного гідроксиапатиту та скла системи $\text{SiO}_2\text{-CaO-Na}_2\text{O}$, на структуру та властивості матеріалу, отриманого методом дублювання структури полімерної матриці. Встановлено, що при спіканні зразків високопористої стеклокераміки при 900°C відбувається часткове розкладання гідроксиапатиту та/або його взаємодія зі склофазою, в результаті чого утворюється багатофазна стеклокераміка, яка містить у своєму складі ренаніт, силікофосфат кальцію, пірофосфат кальцію, пектоліт та гідроксиапатит, а при додаванні до складу зразків фтору утворюється також фторапатит. Показано також, що введення фтору дозволяє більш ніж на 30 % підвищити міцність зразків, а також трохи зменшити розчинність *in vitro*.

1. Introduction

Fluorine is known to take an active part in formation of bones, dentine and tooth enamel and to affect the state and growth of hair and nails. Furthermore, it improves blood and immune systems, participates in the skeleton evolution and stimulates reparative processes after bones fracture. At early age man needs fluorine for good and well-timed mineralization of bones and teeth whereas in old age — for preservation of bone mineralization and prevention of osteoporosis which frequently leads to fracture of femur neck and damage of vertebrae. Fluorapatite crystals are isomorphic to hydroxyapatite ones, therefore replacement of the latter with the former induces no changes in the geometry and morphology of the bones and teeth. Moreover, fluorapatite is more thermally and chemically stable as compared to the hydroxyapatite. However, mechanisms of the fluorine influence on the mineralization processes have not elucidated yet. In addition, thanks to fluorine, our organism better assimilates iron and easier releases heavy metal salts and radioactive nuclides. The fluorine standard amount per day for adults is about 0.5–4.0 mg [1–4].

Today hydroxyapatite materials take top positions among materials used in reproducing the bone tissue thanks to their chemical proximity to the inorganic component of the bone tissue [5, 6]. Despite contradictory opinions on the good and harm of fluorine for man [7, 8], fluorine-containing implant materials remain promising concerning patients suffering from osteoporosis.

Our previous works [9–11] were devoted to the effect of the initial composition and sintering temperature on the structure and properties of highly-porous glass ceramics (HPGC) obtained *via* method of doubling the structure of polymer matrix based on biogenic hydroxyapatite (BHA) and glass of $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ system. It was established that optimal sintering temperature for production of the HPGC with required structure and mechanical characteristics is about 900°C; herein initial composition of the material must contain 50–60 mass% of the BHA. An increase in the initial BHA content from 50 to 60 mass% was shown to raise the efficiency of cloning osteogenic cells (precursors of marrow) by 30 % in the presence of biomaterials [12].

As known from glass melting practice, fluorine introduction into glass composition promotes the appearance of a liquid phase at reduced temperatures and accelerates the

glass-forming processes, which makes it possible to decrease the glass melting temperature by 100–200°C. It also allows one to produce the fluorapatite bioceramics with improved mechanical and biochemical properties [3, 13].

Thus the aim of the present work is to study the fluorine effect on structure and properties of HPGC on the basis of BHA (60 mass% in initial composition) and glass of $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ system.

2. Materials and methods

To produce the permeable bioceramics, BHA, glass of $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ system and foamed polyurethane matrix were used as initial materials. The BHA/glass mass ratio was 60/40. The BHA was obtained via annealing bones of beeves at 900°C. The glass was melted at 1100°C. For comparison, 0.3 mass.% fluorine (relative to glass ceramic composition) was introduced in the form of sodium fluoride (chemically pure NaF "Khimloborre-actiue") in order to accelerate the glass melting process [14] as well as to study the effect of fluorine on the properties of the materials obtained. HPGC samples were fabricated by techniques for doubling the structure of polymer matrix described in the paper [15] using foamed polyurethane ST 3542 ("Interfom", Ukraine) with permeable pore structure (porosity 95 %), which was saturated with slurry on the basis of water with a solid phase content of 60 mass.%. The slurry-saturated matrix was dried and then subjected to heat treatment in a muffle furnace up to maximal temperature of 900°C.

Phase composition of the fabricated samples was controlled by XRD method using diffractometer Ultima IV (Rigaku, Japan). The materials were also studied by IR spectroscopy on a Fourier-spectrometer FSM 1202 (Ltd. "Infraspectr", Russia) in the frequency range of 4000–400 cm^{-1} . The pore structure of the glass ceramics was examined by scanning electron microscopy (microscope REM-106I, Selmi, Ukraine) added with data processing using the specialized material science complex for analysis of structure images SIAMS-600 ("SIAMS-Ltd", Russia). In addition, there was determined their volume shrinkage upon sintering as well as porosity and uniaxial compression strength on a universal machine Ceram Test System ("SD&TB IPS NAS of Ukraine", Ukraine). To estimate bioresorption of the materials, some experiments *in vitro* were conducted, in particular estimation of solubility in isotonic saline (0.9 % NaCl water solution) at $36.5\pm 0.5^\circ\text{C}$ for 2 days.

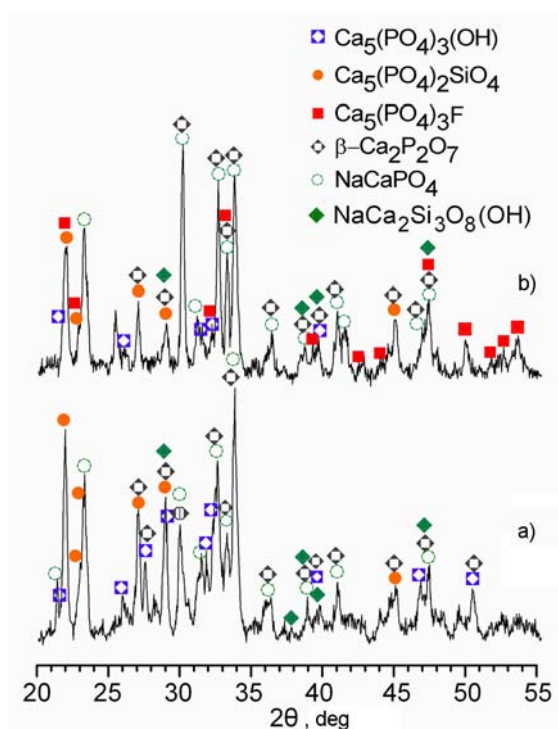


Fig. 1. XRD analysis results for HPGC samples obtained on the basis of (a) fluorine-free and (b) fluorine-containing glass.

3. Results and discussion

Fig. 1 demonstrates XRD data for the biomaterials. As seen, during sintering of the HPGC samples a partial decomposition of the BHA and/or its interaction with the glass phase occur, which results in forming the glass ceramics containing renanite NaCaPO_4 (JCPDS, Card No. 76-1456), calcium silicophosphate $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ (JCPDS, Card No. 21-0157), calcium pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$ (JCPDS, Card No. 33-0297), pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ (JCPDS, Card No. 02-0759) and hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS, Card No. 09-432). Besides, in the samples prepared using the fluorine-containing glass, formation of fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$ (JCPDS, Card No. 02-0845) was observed alongside with changes in the intensity of the main peaks of the above phases. Because of overlapping the XRD peaks of the main phases it is difficult to unambiguously interpret the composition of glass ceramics obtained.

The XRD results are also confirmed by IR spectroscopy data presented in Fig. 2. The latter demonstrates the presence of vibrations of PO_4^{3-} and SiO_4^{4-} groups in the frequency region $\nu \sim 1250\text{--}450\text{ cm}^{-1}$ for the HPGC based on fluorine-free glass [9, 10]. The IR adsorption bands indicate the pres-

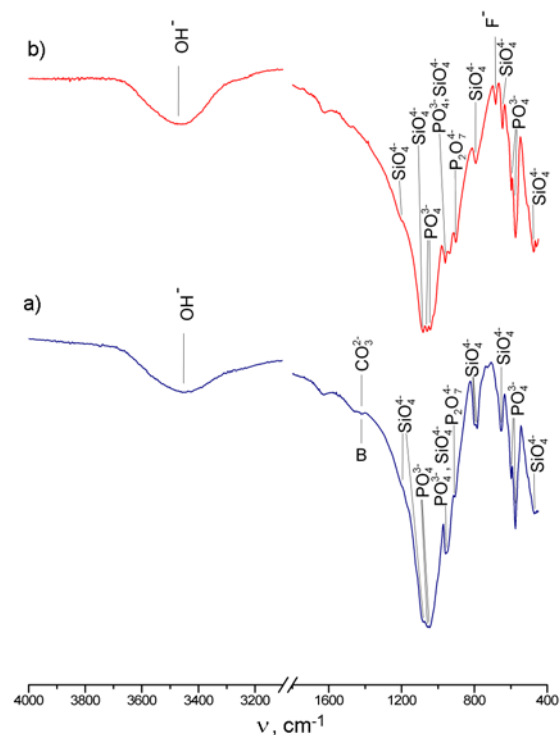


Fig. 2. IR spectra of HPGC materials based on (a) fluorine-free and (b) fluorine-containing glass.

ence of such phases as pyrophosphate, calcium silicophosphate, renanite and hydroxyapatite. In the range of $810\text{--}780\text{ cm}^{-1}$ a doublet is revealed which is typical for silicon-oxygen tetrahedrons and evidences to the presence of rings from six SiO_4 tetrahedrons [Si_6O_{18}] in the glass phase structure that confirmed by the literature data [18]. The absorption bands within $\nu \sim 1040\text{--}900\text{ cm}^{-1}$ characterize the presence of wollastonite structures like pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$. Frequencies in the ranges of $\nu \sim 1200\text{--}900$ and $700\text{--}450\text{ cm}^{-1}$ are connected to the calcium silicophosphate and pyrophosphate phases. Our previous work [10] contains more detailed description of the structure and related frequencies.

Introduction of fluorine into the HPGC provokes changes in the phase composition. The absorption bands within $\nu \sim 1400\text{--}700\text{ cm}^{-1}$ broaden. Peculiarity of phase formation in such a system is the formation of fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$, which is demonstrated by the change in the absorption band $\nu \sim 1200\text{--}650\text{ cm}^{-1}$. Appearance of the additional absorption bands within $\nu \sim 1100\text{--}1000\text{ cm}^{-1}$ and at 682 cm^{-1} may be prescribed to fluorapatite formation [16–18]. Herein the separate band ($\nu \sim 793\text{ cm}^{-1}$) in

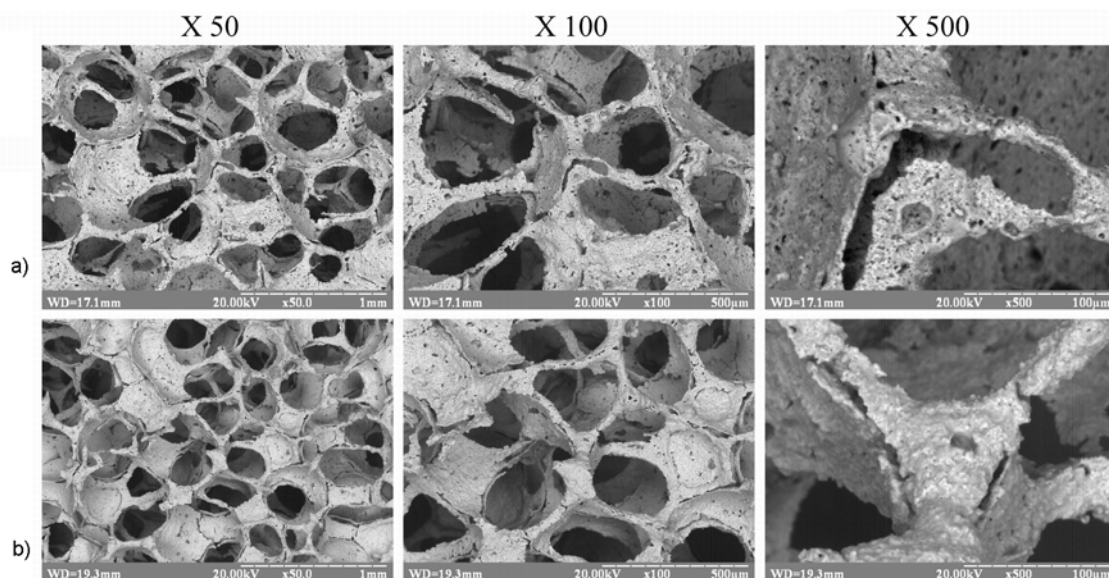


Fig. 3. Structure of HPGC obtained on the basis of (a) fluorine-free and (b) fluorine-containing glass.

the range of $\nu \sim 810\text{--}780\text{ cm}^{-1}$ in contrast to the HPGC based on fluorine-free glass is connected to the SiO_4^{4-} groups. These data indicate the fact that the presence of fluorine blocks the formation of ring structures which possess bioactive properties. Formation of the structures composed of tetrahedrons and chains (phases of calcium pyrophosphate, calcium silicophosphate, renanite and fluorapatite) allows one to control bioresorption properties of the composites.

In addition, in the IR spectra of the materials of both types one can see bands of OH^- vibrations: valence vibrations within $\nu \sim 3600\text{--}3400\text{ cm}^{-1}$ and deformation vibrations with $\nu \sim 1630\text{ cm}^{-1}$. At the same time, the IR spectra of HPGC on the basis of fluorine-free glass contain absorption bands intrinsic to the carbonate-ions CO_3^{2-} in B-positions when they replace PO_4^{3-} groups. The absence of absorption bands intrinsic to the carbonate-ions CO_3^{2-} for fluorine-containing HPGC could be attributed to more complete decomposition of carbonates during the glass melting, which is a result of the intensification of the processes of glass- and silicate formation in the fluorine-containing

glass, as well as a better glass degassing and removing dissolved gases [19, 20].

Table lists the data on volume shrinkage of the samples obtained. As seen, the presence of fluorine does not significantly affect the material sinterability and porous structure. The slight increase in the volume shrinkage of the fluorine-containing HPGC may be related to some factors. On one hand, that is connected to the phase transformations occurring in the material during sintering. On the other hand, the fluorine-containing glass is characterized by lower viscosity [14, 21, 22], which, in its turn, promotes better wettability and densification of material through the liquid phase sintering. This is in a good agreement with the results for the total and open porosity of the samples (Table). The fluorine-containing sample preserves an open pore structure, which is one of the key requirements for the HPGC implant materials.

The structure of the HPGC samples is shown in Fig. 3. As seen, a channel structure with open interacted pore system characterized by the presence of arc-like separation walls, which prevent from formation of

Table. Properties of HPGC samples

Sample type	Volume shrinkage, %	Porosity, %		Strength, MPa	Dissolution rate, mass.%/day
		Open	Total		
F-free	9	76	81	0.9	0.50
F-containing	11	70	77	1.2	0.47

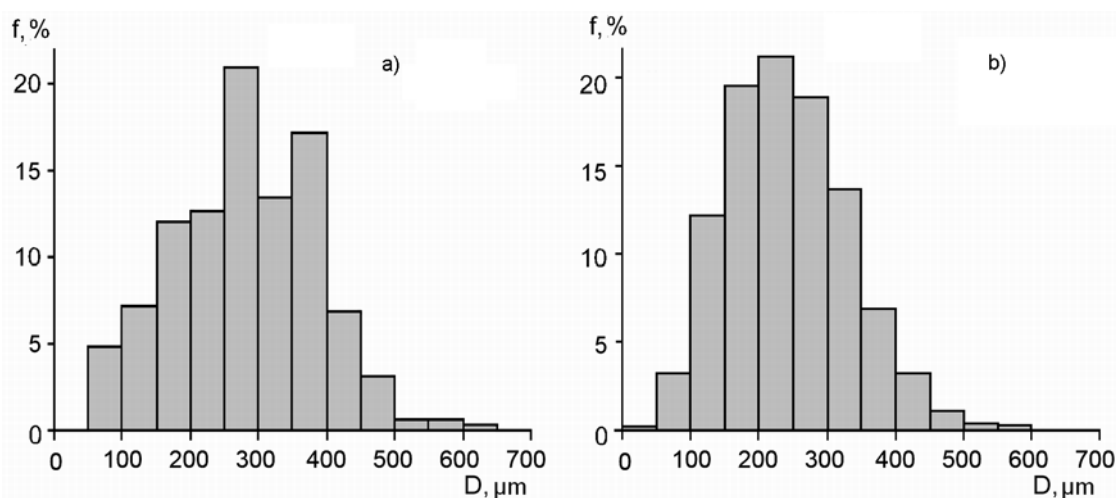


Fig. 4. Pore size distribution in the structure of HPGC obtained on the basis of (a) fluorine-free and (b) fluorine-containing glass.

completely closed cells and disconnected volumes in the material, remains in the samples. As a result of the sintering, both large macropores and small micropores are formed. The structure of the samples prepared from fluorine-containing glass is characterized by vitrification of the pore walls (seen at a magnification of X 500), which is associated with the glass viscosity decrease after the fluorine introduction.

It was established on the basis of analysis of the pore structure (pore size distribution) of the samples of different compositions (Fig. 4) that for fluorine-free glass ceramics the most probable pore size (namely 21 % of the total pore number) is 275 μm ; herein the range in which predominant quantity of the pores falls (~ 75.5 %) is 150–400 μm , whereas for the fluorine-containing samples these values are 225 μm (21 %) and 100–350 μm (86 %), respectively. Besides, the latter contain smaller pores (<50 μm) as compared to the fluorine-free ceramics whose minimal pore size is ~ 50 μm . Such changes in the pore structure of the glass ceramics from fluorine-containing glass are associated with decrease in the glass mass viscosity and phase transformations during interaction of the glass fluorine with hydroxyapatite, which, in its turn, decreases the sintering temperature thanks to liquid phase and reaction types of the sample sintering.

Furthermore, it was established that introduction of fluorine leads to increase in the samples strength by over 30 %. In our opinion, this may be due to the liquid phase sintering and phase transformations induced by the glass-hydroxyapatite interac-

tion in the material, as well as the formation of fluorapatite, that strengthens the glass ceramics in agreement with the literature data [3, 23].

The investigation results of for the rate of HPGC dissolution in saline are presented in Table. The slight decrease in the solution rate for the samples obtained on the basis of fluorine-containing glass is related to the presence of fluorapatite formed due to sintering and phase transformations, which is less soluble than hydroxyapatite.

4. Conclusions

The effect of fluorine on the structure and properties of the highly-porous glass ceramics obtained via doubling the polymer matrix structure on the basis of biogenic hydroxyapatite and glass of $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ system was investigated. It was established that during sintering a partial decomposition and/or interaction of hydroxyapatite with the glass phase take place, which results in forming the multiphase ceramics composed of renanite, calcium silicophosphate, calcium pyrophosphate, pectolite and hydroxyapatite. Also, in the case of fluorine introduction into the highly-porous glass ceramics samples, fluorapatite is present. Besides, introduction of fluorine was shown to increase the strength of the permeable open-pore-structured samples by 30 %. Furthermore, it slightly decreases the solubility *in vitro*, which makes it possible to control resorption properties of the implant materials and in such a way to make them promising for treatment of the bone tissue diseases in orthopedy and traumatology.

References

1. E.T.Everett, *J. Dent. Res.*, **90**, 552 (2011).
2. M.Supova, *Ceram. Int.*, **41**, 9203 (2015).
3. F.A.Shah, *Mater. Sci. Eng. C*, **58**, 1279 (2016).
4. A.Bianco, I.Cacciotti, L.Montanaro et al., *Ceram. Int.*, **36**, 313 (2010).
5. M.Sadat-Shojai, M.-T.Khorasani, E.Dinpanah-Khoshdargi, A.Jamshidi, *Acta Biomater.*, **9**, 7591 (2013).
6. M.Vallet-Regi, *Compt. Rend. Chim.*, **13**, 174 (2010).
7. J.Aaseth, M.Shimshi, J.L.Gabrilove, G.S.Birketvedt, *J. Trace Elem. Exp. Med.*, **17**, 83 (2004).
8. P.Vestergaard, N.R.Jorgensen, P.Schwarz, L.Mosekilde, *Osteoporos. Int.*, **19**, 257 (2008).
9. A.Iatsenko, O.Sych, T.Tomila, *Proc. Appl. Ceram.*, **9**, 99 (2015).
10. E.E.Sych, A.P.Yatsenko, T.V.Tomila et al., *Powder. Metall. Met. Ceram.*, **55**, 319 (2016).
11. Ukraine Patent 92619 (2014).
12. L.M.Panchenko, E.E.Sych, A.P.Iatsenko, *Bullet. Ortop. Traumatol. Pros.*, **4**, 50 (2014).
13. D.S.Brauer, M.N.Anjum, M.Mneimne et al., *J. Non-Cryst. Solids*, **358**, 1438 (2012).
14. M.Plemyannikov, A.Iatsenko, B.Kornilovych, *Glass Chemistry and Technology. High Temperature Processes*, Osvita, Kyiv (2015) [in Ukrainian].
15. Ukraine Patent 97215 (2015).
16. Mahmoud Eidi, *Ind. J. Fund. Appl. Life Sci.*, **4**, 3690 (2014).
17. B.Basar, A.Tezcaneer, D.Keskin, *Z. Ceram. Int.*, **36**, 1633 (2010).
18. I.I.Plyusnina, *Infrakrasnye Spektry Silikatov*, Izdatelstvo Moskovskogo Universiteta, Moscow (1967) [in Russian].
19. Yu.A.Guloyan, *Tehnologiya Steklotary i Sortovoy Posudy*, Legprombytizdat, Moscow (1986) [in Russian].
20. M.A.Bezborodov, *Sintez i Stroenie Silikatnyh Styokol*, Nauka i Tehnika, Minsk (1968) [in Russian].
21. N.M.Pavlushkin, *Himicheskaya Tehnologiya Stekla i Sitallov*, Stroyizdat, Moscow (1983) [in Russian].
22. V.V.Pollyak, P.D.Sarkisov, V.F.Solinov, M.A.Tsaritsyin, *Tehnologiya Stroitel'nogo i Tehnicheskogo Stekla i Shlakositallov*, Stroyizdat, Moscow (1983) [in Russian].
23. F.Barandehfard, M.Kianpour Rad, A.Hosseinia et al., *Ceram. Int.*, **42**, 17866 (2016).