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## INVESTIGATION OF PHASE SEPARATION PROCESSES FOR BIOACTIVE GLASSES IN $\text{Na}_2\text{O}-\text{CaO}-\text{ZnO}-\text{TiO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ SYSTEM

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**Abstract.** Nanostructural changes on initial stages of calcium silicophosphate glasses nucleation in  $\text{Na}_2\text{O}-\text{CaO}-\text{ZnO}-\text{TiO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  system during phase separation have been investigated. It has been established that the presence of drop-shaped nano- and micro-nonuniformities in the structure of calcium silicophosphate glasses substantially affects the glass separation in a precrystallization period, helping intense fine hydroxyapatite crystallization with the crystal size of up to 1  $\mu\text{m}$  after heat treatment.

**Keywords:** nanostructure, liquation, calcium silicophosphate glass-ceramic materials, bone endoprosthetics.

### 1. Introduction

Today the possibilities of multivariable application of nanotechnologies in the field of medicine, biology, chemical technology and other industrial areas allow resolving complicated scientific and technical tasks related to the development of implants for bone prosthetics.

Processes of self-organizing in creating specific dissipative structures both during the nucleation stage and in the further evolution play an important role in the development of new generations of functional bioactive materials [1]. Main aspect of synthesis of biocompatible fine crystalline calcium silicophosphate glasses and material on their base is the provision of the uniform fine volume crystallization of calcium phosphates, in particular, through liquation mechanisms of nucleation [2], as the formation of nonuniformities helps the following layering of glass in the precrystallization period [3]. The need for the highly arranged self-organizing nanoscale structure of calcium phosphate materials is an important factor, needed for provision of their medical,

biological, chemical, mechanical and engineering properties [3, 4].

It is well known that nanostructuring in glasses and glass-ceramic materials occurs *via* crystallization of amorphous structures by statistical nucleation of nano-clusters with their following growth [5]. The primary layering has been considered by W. Vogel as a prerequisite of homogeneous appearance of crystalline centers that leads to the following controlled crystallization [6]. F. Galakhov *et al.* [6, 7] have established that the cause of uniform crystallization without catalyst impurities present is the layering of primary melt into immiscible phases in the form of parts or drops of extremely small sizes which are unable to increase their size microliquation. According to W. Vogel, the formation of the small drop-shaped regions of immiscibility is the initial stage and prerequisites for crystallization from the considerations that the composition of these drops is close to that of the stable crystalline phases. V. Filippovich has the different view upon this problem. He questions the assumption of necessary existence of precrystallization liquation – due to the phase separation, phase interface boundaries become significantly developed and facilitate diffusion processes resulting in the glass composition close to the one of future crystals.

Main reason of liquation in oxide glasses is the electrostatic force interaction between the melt ions and related tendency of modifier cations and glass forming cations to surround themselves with oxygen ions in accordance with their coordination numbers conditioned by the crystal-chemical conditions. The bigger the cation field strength, the stronger are the tendencies for liquation. It is known that calcium silicophosphate glasses have wide liquation regions. Mechanism of  $\text{P}_2\text{O}_5$  action as a crystallization catalyst is based on the division of the system into two liquid phases. Phosphorous anhydride is

built up into the glass forming network and it creates the conditions for the cleavage of Si-O-Si bonds as the double bond of phosphorous with oxygen is created. This bond differentiates tetrahedra  $[\text{PO}_4]$  from  $[\text{SiO}_4]$  [8].

Development of bioactive calcium silicophosphate glass-ceramics of biomedical purpose includes creation of a glass matrix with a developed liquation structure, which creates heterophase fluctuations with subsequent formation of crystalline phases of calcium phosphates, responsible for bioactivity. The main factor determining crystallization ability of experimental glasses is the content and ratio of CaO and  $\text{P}_2\text{O}_5$  as well as the presence of crystallization catalysts.

Purpose of this work is to investigate the nanostructural changes at the initial stages of nucleation in calcium silicate glasses containing crystallization catalysts:  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{ZnO}$ .

## 2. Experimental

To study nanostructure of calcium silicophosphate glasses obtained BS-5 and BS-11 glasses of  $\text{Na}_2\text{O}-\text{CaO}-\text{TiO}_2-\text{ZrO}_2-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  system with a respective ratio of  $\text{CaO}/\text{P}_2\text{O}_5$  1.5 and 4, as well as glass ZF-1 synthesized in  $\text{Na}_2\text{O}-\text{CaO}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  system with the ratio of  $\text{CaO}/\text{P}_2\text{O}_5 = 4$  have been chosen. All model glasses are located in the high-silica region with the content of  $\text{B}_2\text{O}_3$  5 mol %, the content of  $\text{Na}_2\text{O}$  for BS-11 and ZF-1 is 10 mol %, for BS-5 it is 15 mol %.

The choice of the compositions of model glasses was also based on the possibility to establish the effect of crystallization catalysts on the liquation processes in calcium phosphate glasses. In the composition of BS-5 and ZF-1 model glasses the catalysts amounts of 5 mol %  $\text{ZrO}_2$  and 5 mol % of  $\text{ZnO}$  have been added. In BS-11 the glass crystallization catalyst has been replaced by  $\text{Al}_2\text{O}_3$ .

All studied glasses in  $\text{Na}_2\text{O}-\text{CaO}-\text{ZnO}-\text{TiO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  system were melted under identical conditions at the temperatures of 1673–1773 K in corundum crucibles with the subsequent quenching on the metal plate.

Structure of glasses has been studied with an electron microscope “Tesla” with the aninitial magnification of 2500–3000 and by infrared spectroscopy using film deposition method in the oscillations interval of 4000–400  $\text{cm}^{-1}$  with Specord-80. Identification of the crystalline phase in the model glasses has been conducted with x-ray diffraction analysis, which has been carried out on the DRON-3 apparatus. Petrographic studies have been carried out with an optical microscope MIN-8.

## 3. Results and Discussion

Investigation of nanostructural changes at the initial stages of nucleation in calcium phosphate glasses is an important stage in developing bioactive apatite-containing glass-ceramic materials with a fine structure.

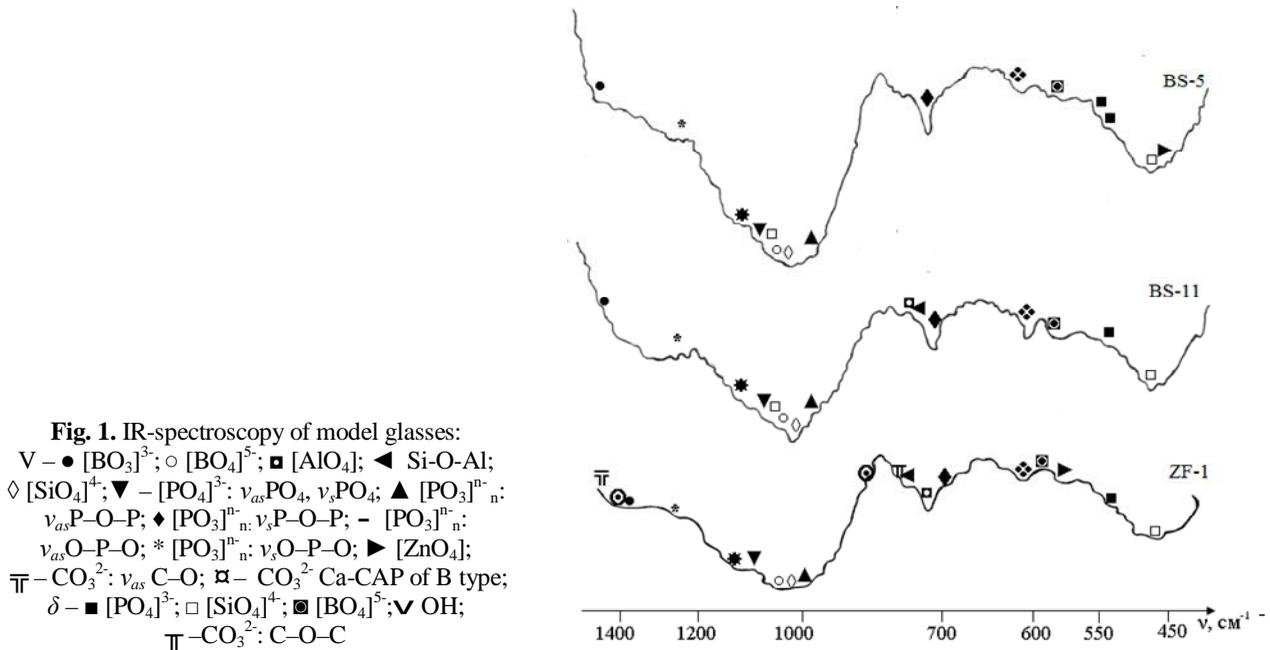
According to IR data model glasses BS-5, BS-11, ZF-11 with the content of  $\text{SiO}_2 > 50$  mol % are characterized by the wide absorption band ( $V$ ) of valence oscillations ( $\nu$ ) in the region of 900–1200  $\text{cm}^{-1}$  with a deep minimum at 1050  $\text{cm}^{-1}$ , and deformation oscillations ( $\delta$ ) at 470  $\text{cm}^{-1}$ , which is the evidence of high polymerization extent of  $[\text{SiO}_4]$  tetrahedra (Fig. 1).

Presence of  $\text{Al}_2\text{O}_3$  in model glasses BS-11, ZF-1 conditions the formation of three-dimensional network with  $[\text{AlO}_4]$  and  $[\text{SiO}_4]$  groups. The presence of Si-O-Al bond in the glasses is evident from the absorption band in the region of 720–780  $\text{cm}^{-1}$ . The absence of oscillation in the region of 580–680  $\text{cm}^{-1}$  in model glasses, which are characteristic for octahedra  $[\text{AlO}_6]$ , also indicates that aluminum is in fourfold coordination in the region of 710–780  $\text{cm}^{-1}$ , isomorphically substituting silicon and forming the mixed aluminium-silicon-oxygen network. In the model glasses BS-11, BS-5, ZF-1 valence oscillations of  $[\text{BO}_3]^{3-}$  with the absorption band at 1350–1400  $\text{cm}^{-1}$  have unclear character, implying more characteristic tetrahedral coordination of boron for model glasses. For ZF-1 glass, the presence of tetrahedral zinc-oxygen complexes is typical, with the absorption maximum in the region of 400–650  $\text{cm}^{-1}$ .

For model glasses with  $\text{P}_2\text{O}_5$  amount from 5 to 10 mol % symmetrical oscillations of bridges P-O-P are clearly evident. They reside in a wide frequency interval, providing the possibility of each oscillation band identification for  $[\text{PO}_3]^{n-}$  anion. Glass spectra contain metaphosphate groups  $[\text{PO}_4]^{3-}$ , indicating the formation of sybotaxic groups of future nucleators of phosphates in them during cooling, and the presence of phosphates in the structure of glass

According to IR-spectroscopy data, the absorption maximum of deformation oscillation of OH group in the region of 630  $\text{cm}^{-1}$ , is characteristic of all glasses, which is an evidence of Ca-HAP crystallization. Crystallization of Ca-CAP of B type is corroborated by the presence in ZF-1 glass spectra  $\nu_{as} \text{CO}_3^{2-}$  bridges C-O in 1600–1400  $\text{cm}^{-1}$  region and  $\delta$  bridges of C-O-C in 880–870  $\text{cm}^{-1}$  region.

Identification of Ca-CAP of A type is complicated by the superposition of intrinsic valence oscillation of  $\text{CO}_3^{2-}$  groups of C-O bridges in 1450–1460, 1540–1570  $\text{cm}^{-1}$  regions with  $\text{CO}_3^{2-}$ , intrinsic oscillations for Ca-CAP of B type.



Results of XRD (Fig. 2) and petrographic analyses have shown that studied glasses have calcium hydroxyapatite (Ca-HAP) as a main crystalline phase. For BS-11 glass, the presence of Ca-HAP after melting is about 30 % with the size of its crystals up to 1 μm; for ZF-1 glass, joint amount of Ca-HAP and Ca-CAP has the same value as the aforementioned one for the crystal size of 0.5–1 μm, with the phase ratio Ca-HAP/Ca-CAP being 2/1 [9, 10]. For the glass BS-5, opalescent after melting, the amount of Ca-HAP is significantly less and is only 10 % with the size up to 3 μm.

Thus, ensuring the ratio CaO/P<sub>2</sub>O<sub>5</sub> = 4 in the experimental glasses BS-11 and ZF-11 allows achieving fine crystallization of Ca-HAP and Ca-CAP as the necessary condition of their bioactivity *in vivo*. Decrease of CaO/P<sub>2</sub>O<sub>5</sub> ratio to 1.5 leads to the reduction of the quantity of Ca-HAP crystalline phase in its structure decreasing its reactivity. Introduction of ZrO<sub>2</sub> into BS-5 glass composition stipulate the increase of Ca-HAP crystalline phase quantity to 8 μm after thermal treatment, introduction of ZnO into ZF-1 glass composition, on the contrary, leads to the decrease of Ca-HAP crystalline phase size to 1 μm.

According to data of the electron microscopy the surface of BS-11 glass after melting is micro-nonuniform (Fig. 3a). It has components of different structure and size. Components are presented by glass, confined particles with size of about 1 μm, as well as by separate and elongated prismatic particles with sizes of 0.1×0.5 μm that randomly pierce the matrix base. The inside liquation occurs within the confined particles with the size of nonuniformities of 0.01–0.05 μm with subsequent structure arrangement process. The appearance of the

secondary hemisphere-shaped layering in the test glasses is the evidence of the completion of the phase separation process in the glass. Lack of clear edges of spherical formations with the presence of elongated prismatic particles with the size of 0.5 μm the phase boundary at the further increase (Fig. 3b) of the glass is the evidence of heterogeneous nucleation of Ca-HAP, which is confirmed by XRD data.

The structure of BS-5 specimen is characterized by the presence of glass matrix and long blocks 1.0–1.5 μm length, oriented towards the front of crystallization, on which, in turn, drop-shaped entities of 0.08 μm occur (Fig. 4a). Blurred edges of the blocks are explained by the presence of thin glass phase layer on them. Besides, at further magnifications, processes of phase separation occur in the form of nonuniform clusters of different shapes as well as prismatic particles with the size of 0.5–1 μm (Fig. 4b).

Microstructure of ZF-1 specimen has a nonuniform distribution of clear drop-shaped particles with the size of 0.5–1 μm (Fig. 5a). Treatment of the glass specimen in HF allowed observation of uniformly distributed particles on its fracture with the size of ≈ 0.1 μm (Fig 5b), as well as separate spherical formations with the size of about 0.01 μm, that can be an evidence of the inner liquation process with further structure.

Needle-shaped crystals in Fig. 5c are the evidence of the presence both HAP and A-type CAP. Introduction of carbonate-containing raw material – chalk, into the composition of ZF-1 glass in the amount of 12 mas % allows crystallization of mixed A-B type Ca-CAP approximating the material by its composition to the young living bone.

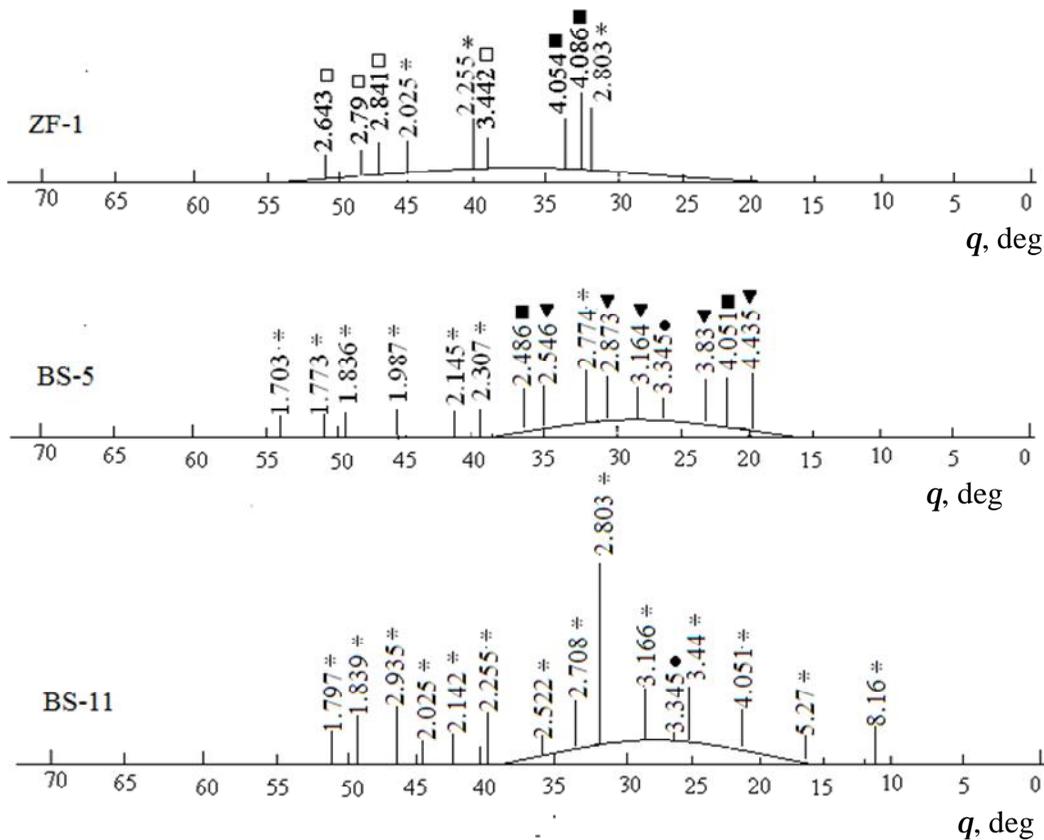


Fig. 2. X-ray diffraction of glasses: ● – quartz, ■ – cristobalite, ▼ – CaZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>, □ Ca-CAP, \* – Ca-HAP

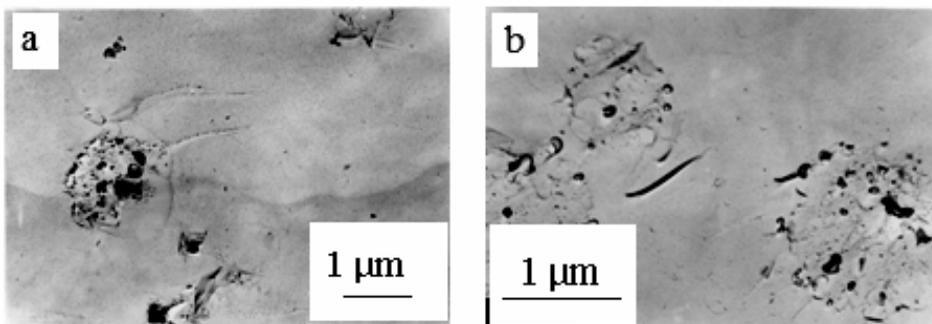


Fig. 3. SEM pictures of BS-11

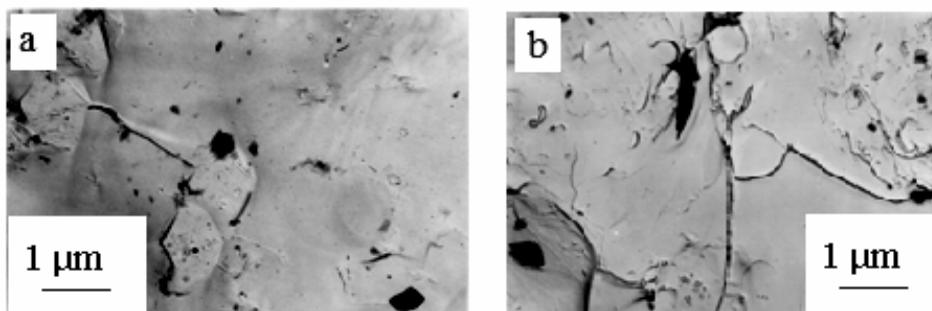


Fig. 4. SEM pictures of BS-5

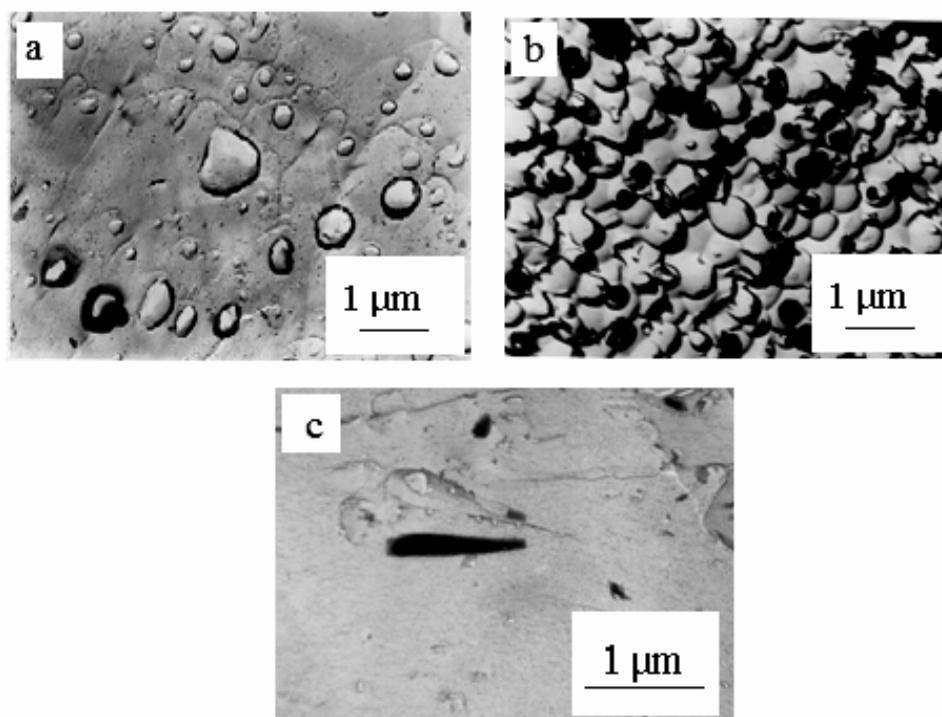


Fig. 5. SEM pictures of ZF-1

As it has been shown by studying the structure of tested phosphate glasses, the complex character of liquation processes is a common feature for them irrelevantly of the presence of crystallization catalyst and CaO/P<sub>2</sub>O<sub>5</sub> ratio, which is expressed by formation of nanospherical nonuniformities including inside micro drops.

Occurrence of the secondary layering of spherical formations with the size of 0.01–0.08 μm in tested glasses as a stage of heterogeneous nucleation, is related with the formation of stabilized clusters – heterophase fluctuations creating the self-arranged structure. Introduction of ZnO into the composition of phosphate glasses leads to the intensive process of phase separation in the form of nano- and micro-nonuniformities formation in the glass structure with subsequent nucleation and appearance of crystal phase with the size up to 1 μm. Introduction of ZrO<sub>2</sub> into the composition of tested glasses along with the liquation process conditions the formation of significant quantity of crystalline phase with the size up to 3 μm after melting with its subsequent growth, which in turn can negatively affect the structure strength and increase solubility of the material.

#### 4. Conclusions

On the basis of investigations of phase separation features in glasses of Na<sub>2</sub>O–CaO–ZnO–TiO<sub>2</sub>–ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub> system, it has been established

that the formation of spherical nano- and micro-nonuniformities leads to the drop liquation with subsequent occurrence of sybotaxic groups of future crystalline calcium phosphates and nucleator phases during model glasses melting, and calcium phosphates during their cooling. Formation of nanoscale secondary layering in the evenly distributed nonuniformities in the structure of model glasses leads to subsequent structure ordering with Ca-HAP and mixed A-B type Ca-CAP crystallization, approximating the composition of glass to the one of a young bone tissue.

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**ВИВЧЕННЯ ПРОЦЕСІВ ФАЗОВОГО РОЗДІЛЕННЯ  
В БІОАКТИВНОМУ СКЛІ СИСТЕМИ  $\text{Na}_2\text{O}-\text{CaO}-$   
 $\text{ZnO}-\text{TiO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$**

*Анотація.* Досліджено наноструктурні зміни на початкових стадіях зародкоутворення в біоактивному кальцій-

силікофосфатному склі системи  $\text{Na}_2\text{O}-\text{CaO}-\text{ZnO}-\text{TiO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$  в процесі фазового розділення. Встановлено, що присутність краплеподібних нано- і мікронеоднорідностей в структурі кальційсилікофосфатного скла має суттєвий вплив на розширення скла в докристалізаційному періоді, що сприяє інтенсивній тонко дисперсній кристалізації гідроксиапатиту з розміром кристалів до 1 мкм після термооброблення.

**Ключові слова:** наноструктура, ліквіація, кальцій-силікофосфатний скло-керамічний матеріал, ендопротезування кісток.