

RIGA TECHNICAL UNIVERSITY
Faculty of Materials Sciences and Applied Chemistry
Institute of General Chemical Engineering



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**CRYSTALLIZATION OF GLASS IN
 $\text{Na}_2\text{O-CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$ SYSTEM**

Summary of Doctoral Thesis

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**DOCTORAL THESIS
SUBMITTED IN RIGA TECHNICAL UNIVERSITY
FOR ACQUISITION OF THE
DOCTORAL DEGREE IN ENGINEERING SCIENCES**

Doctoral thesis are openly defended on October 25, 2012 at 15.00 in Riga Technical University Faculty of Material Sciences and Applied Chemistry lecture room 272 (14/24 Āzenes Str.).

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CONFIRMATION

Hereby, I confirm that I have worked out the current Doctoral Thesis, which is submitted for consideration in the Riga Technical University for acquisition of Doctoral degree. Current scientific thesis is not submitted in other scientific institutions for acquisition of the scientific degrees.

Agnese Stunda-Zujeva

Date:

The thesis is written in Latvian, includes introduction, materials and methods, results and discussion, conclusions, bibliography with 81 sources. Thesis is on 124 pages, contains 65 figures and 10 tables.

State Of The Art

The investigation and control of glass crystallization is a key factor for developing new glass-ceramic materials. In this work the usage of several analytical methods (X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM)) for glass crystallization was studied. Optimum operating parameters and the impact of parameters of the equipment/material on the results of the analysis were determined. It is crucial for higher resolution and correct interpretation of raw data that is especially important for poorly crystalline multiphase materials with these methods.

Calcium phosphate biomaterials are promising materials for bone tissue replacement; however, often contradictory qualities are required, such as high solubility and mechanical strength. This problem could be addressed through the use of composite materials such as glass-ceramics. Glass-ceramic composition is adjustable over a wide range, glass and crystalline phases as well as microstructure are variable, which allows the development of materials with different characteristics. However, the crystallization of phosphate glass systems has been little studied and the properties of glass and glass crystallization processes can be significantly affected by even small changes in the glass qualitative and quantitative composition. In this work glass forming ability and crystallization processes of system $\text{CaO-Na}_2\text{O-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$, as well as the various aspects of the biocompatibility of glass-ceramics has been studied.

The aim: to study a crystallization of a glass-ceramic in a system of $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ for potential use as biomaterial.

Research Tasks

1. To develop a complex method for glass crystallization investigation, incl. development and validation of X-ray diffraction data collection method for poorly crystalline materials.
2. To study an impact of composition and conditions of crystallization process in a glass system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$.

Scientific Novelty

In a study of glass crystallization process and kinetics a novel composition glass-ceramic in a system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ has been determined:

- glass forming region of system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-8Na}_2\text{O}$,
- impact of various crystallization parameters on a product (glass-ceramic).

Practical Applications

- Determination of regularities of producing and properties of novel composition glass-ceramic in system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ for the potential applications for biomaterials
- A complex method has been developed for investigation of different poorly and semi-crystalline materials: incl. XRD analysis for determination of composition.

Statements to defend

1. The effect of several X-ray diffraction data collection parameters was evaluated. Using appropriate parameters can significantly lower detection limits – lower concentrations and finer crystallites can be analysed.
2. Crystalline phases obtained by slow cooling of melt differ from that obtained by glass reheating. Reheating rate does not affect quantitative composition and sequence of forming crystalline phases.
3. Experimentally proved that the Nb/P ratio in crystalline niobophosphates affects the content of CaO and P_2O_5 in parent glass.
4. Experimentally proved that in a system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ it is possible to obtain composite material that contains easily soluble phase (calcium phosphate) and poorly soluble and mechanically strong phase (niobophosphates).

LITERATURE REVIEW

Glass-ceramics is a relatively new class of materials that demonstrate the unique combination of properties and has rapidly become an indispensable in everyday life and technology, however, the use of glass-ceramic implant materials is not yet popular. Glass-ceramics is obtained by crystallization of glass; the properties of glass-ceramic and corresponding glass differ significantly. The phenomenon of glass formation is not yet fully understood. There are several theories for predictions of glass-forming ability, but none of them explain glass-forming ability of all compositions. The theory of oxide glass structure states that glass formers make M-O-M-O-M type networks or chains, where M is a cation of glass former, which is connected via oxygen bridge or bridging oxygen. Ionic substances break chains of relatively covalent bonds, these substances are called modifiers. Some elements, such as transition metals, depending on the circumstances and the concentration may be either glass-makers or modifiers.

Glass properties can be mainly explained by the structure of glass network and substructure interactions. P_2O_5 is extremely hygroscopic. Addition of various modifiers can improve the chemical and mechanical strength of phosphate glass. Nb^{5+} easily replaces P^{5+} , thus, a mixed glass network is formed. Nb-O bond is

stronger than P-O bond, so the glass becomes more chemically and mechanically resistant. Niobium as a transition metal with an empty d electron shell gives the glass a variety of optical properties - colour and non-linear light refractive index.

Glass as a category on the theory of crystallization is not covered. Glass crystallization has two mechanisms: surface and volume crystallization, depending on what significantly changes glass-ceramic forming technologies. Crystal growth and morphology are affected by the control of crystallization driving force.

RESEARCH METHODOLOGY AND PLANNING OF EXPERIMENTS

In this work analytical instruments and analytical methods mainly available at RTU Institute of General Chemical Engineering were used: differential thermal analysis, X-ray diffractometer, scanning electron microscope, analytical balance with hydrostatic weighting, etc. Chemical durability was tested according to GOST 10134.1-82, GOST 10134.2-82, GOST 10134.3-82 and ISO 10993-14.

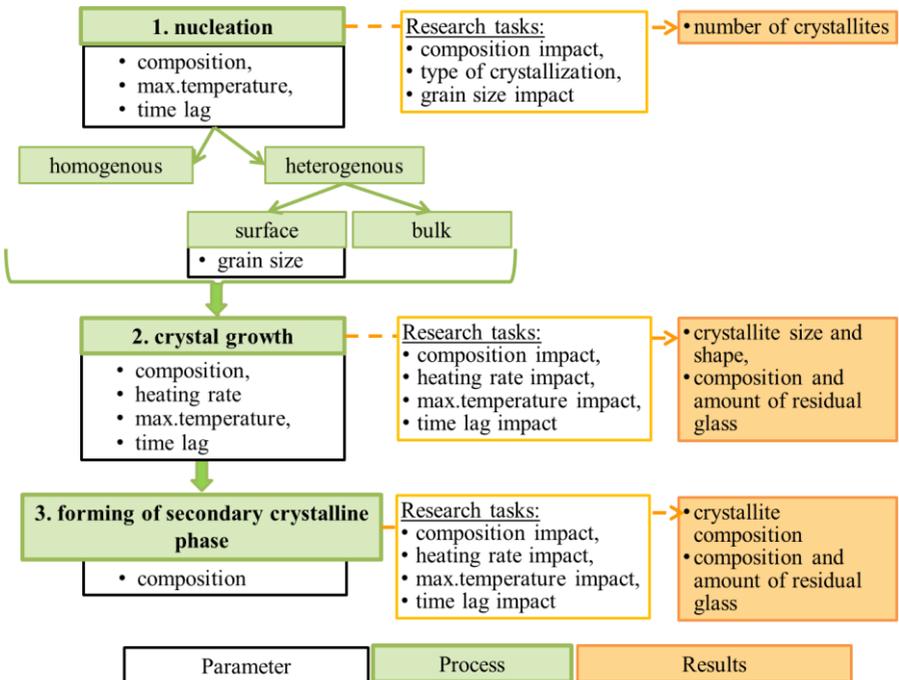


Fig.1. Summary of crystallization theory and relationship studied at each of the stages of crystallization.

Summary of crystallization theory and the relationship studied in this work at each of the stages of crystallization are shown in Fig.1.

RESULTS AND DISCUSSION

1. Evaluation of different analytical methods for the investigation of glass crystallization

The advantages and disadvantages of methods used to develop thesis were identified studying the glass crystallization process. The results are summarised in Table 1.

Table 1

Advantages and disadvantages of analytical methods used in investigation of glass crystallisation and phase analysis of semi-crystalline substances

| Advantages | Disadvantages |
|--|--|
| Differential thermal analysis (DTA) | |
| <ul style="list-style-type: none"> + The method to determine the characteristic temperature of phase transition and thermal effects: T_g, T_c, T_m + Can be used to determine grain size distribution effect on crystallization + One can determine the effects of heating rate on the crystallization temperature. + A small mass of sample (~ 40 mg) | <ul style="list-style-type: none"> – A small mass of sample – Requires additional methods to identify the phase transitions – Cannot determine the process development at constant temperature |
| X-ray diffraction analysis (XRD) | |
| <ul style="list-style-type: none"> + Fast and easy method for identification of crystalline phases, determine average content phases in the sample surface (up to a few micrometers depth) + Can be used to follow the crystallization process: by comparing the sample crystallite size and changes in phase composition + One can observe the crystallite texturing, for example, growth from surface + The sample is not affected by analysis, it may still be used in other experiments + By polishing phase composition can be | <ul style="list-style-type: none"> – The diffraction peaks are wider for smaller crystallites, which may interfere with the identification of phases – Phase composition determination can be difficult for texturized samples – Phase compositions can rarely be unambiguously identified – Diffraction patterns of different crystalline substances can be very similar – Does not give information about |

| Advantages | Disadvantages |
|--|---|
| determined layer by layer from surface across volume | the composition of the amorphous phase |
| Scanning electron microscopy by secondary electron detector (SEM-SE) | |
| + The method for surface morphology analysis | – Pictures are black and white, no recognition of different colourful phases |
| + Images are three-dimensional | – If the surface is smooth, then additional sample treatment can be required, e.g. etching |
| + Extensive microstructure data: sample homogeneity, porosity, and crystallite size, shape and distribution on the surface or fracture (by volume) | – Data interpretation requires experience |
| Scanning electron microscopy by backscattered electron detector (SEM-BSE) | |
| + Method for studying phase microstructure in the plane; the phases with a different density and conductivity are gives different brightness, for example, calcium phosphates can be easily distinguished from niobium containing phases | – Images is not three-dimensional – The sample must be flat – Additional data is required for interpretation of phase composition |
| Scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) | |
| + Method of element analysis; chemical composition of each phase can be determined | – Spot size depends on molecular weight of sample, for lighter phases it is bigger |
| + Composition gradient can be easily determined | – Analysing too small or thin grain, the result can also include the phase composition of the surrounding |
| + The size of analysed phase (grain) may be very small (~ 5-15 nm) | |
| + One can analyse the phases of extremely small concentrations (a few crystallites) | |

1.1 X-ray diffraction analysis parameter impact on determination of poorly crystalline phase composition

The quality of diffraction pattern is based on a sufficient peak height to background fluctuations ratio. Peak height of the material depends on the amount of crystalline phase and crystallite size. Diffraction pattern of a substance which is partially crystalline, or with fine crystallites, gives less intensive and broader peaks

thus pattern is more difficult to interpret. Selecting optimal parameters can significantly improve the resolution of diffraction pattern; thereby study of earlier crystallisation stages can be possible.

Diffraction patterns were taken with PANalytical X'Pert PRO diffractometer. Cu K α radiation at 40 kV and 30 mA was used. X-rays propagation during the measurement and beam limiting slits are shown in Figure 2. In this study the impact of following parameters on diffraction pattern were investigated:

- a) step size,
- b) time per each step or step time,
- c) the various sizes of mechanical and automatic incident and reflected beam adjustment slits.

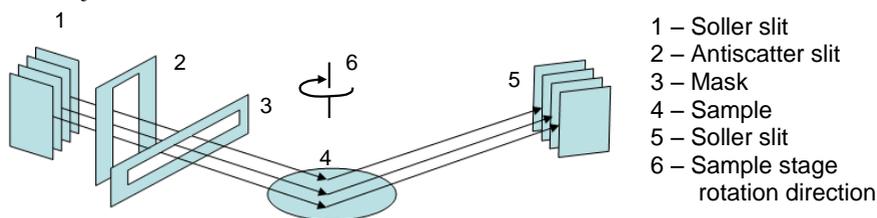


Fig.2. Schematic representation of X-rays propagation in diffractometer

The step size of measurement step must be selected so that the most intensive peaks above the half height have at least 5-10 points. The use of too small step size, can make determination of the exact position of diffraction peak reflex maximum difficult, because the peak top splits (background fluctuations become visible), and the measurement time is significantly increased. Too wide a step size does not improve determination the exact peak position and adjacent peaks may merge together.

Another parameter that affects the overall measurement time is time per step. According to literature increasing the time twice the peak intensity is growing twice while the background intensity of only $2^{0.5}$ times, that is why for well-defined diffraction pattern time per step is very important parameter; however, in scientific publications it is rarely referred.

Experiments with different slits show that wider antiscatter slit in all range steadily increases intensity of diffraction pattern, while the wider mask increases the intensity in large angular area but automatically adjustable slit - in small angular region. Consequently, the various combinations of slits can change the background curvature which can, for example, in quantitative determination of amorphous phase can lead to significant error.

The samples of poorly crystalline material diffractograms are shown in Fig.3. It is clearly visible the using appropriate parameters increase the number of

significant peaks from 7 to 22. Peak is called significant if the intensity of peak is twice of background fluctuations.

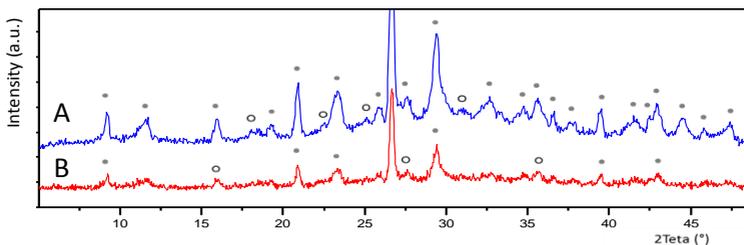


Fig.3. Diffractograms of poorly crystalline material. A – XRD collected using appropriate parameters, B – using parameters appropriate for more crystalline material; • significant peaks, ○ doubtful peaks

2. Glass crystallization kinetics and changes in phase composition

In this part of work the bioactive glass (in system $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$) previously obtained in RTU RBIAC was studied. By using scanning electron microscopy it was found that crystallization of monolithic 8N glass occurs from the surface or the microcracks, as shown in Figure 4.

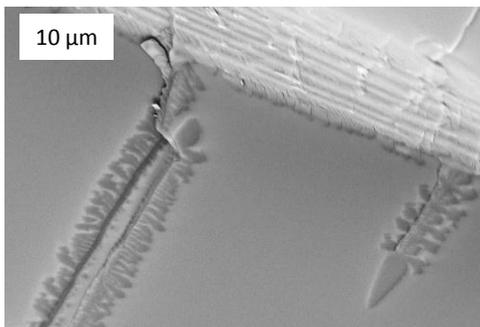


Fig.4. SEM-BSE micrograph. Fracture of partly crystalline monolith glass

Crystallization mechanism may alter, during changes in specific surface area. Therefore by differential thermal analysis, crystallization temperatures were compared for powders with different grain distribution. It was found that the primary crystal phase crystallizes from the surface but the secondary from volume. The granulometry of glass powder is essential for the crystallization process – for fine powders the phase transitions are determined more accurately. For further crystallization investigation the finest 8N glass powder was used (70% of particles are in a range 0.5 – 20 μm).

In DTA it was obtained by increasing the heating rate from 1°C min^{-1} up to $20^\circ\text{C min}^{-1}$ exothermic crystallization peaks shifts to about 100°C higher

temperature (see Fig. 5). Glass stability or interval between softening point and the beginning of crystallization increases with increasing heating rate.

At heating rate of $1^{\circ}\text{Cmin}^{-1}$ $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$ is formed already at 780°C , but at ten times higher heating rate, this phase is formed at 880°C . In addition, increasing the difference between phase transitions in DTA sample (0.04 g) and the XRD sample (0.3 g), could be explained, with the different sample size and the crystallization conditions. The samples for XRD analysis are heated in the crucible, filled with powder to reduce temperature gradient in the sample. Thus, at higher heating rates is likely that crucible slows heat flow to sample and it does not reach the required temperature.

The impact of time lag. The samples heated with $1^{\circ}\text{C min}^{-1}$ up to 770°C without retention at maximum temperature are X-ray amorphous. After 10 minutes at 770°C $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$ are formed. After 60 minutes $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$ are formed and niobate content already is small. Phase transitions at different heating rates, maximum temperature and various time lags are summarized in Figure 5.

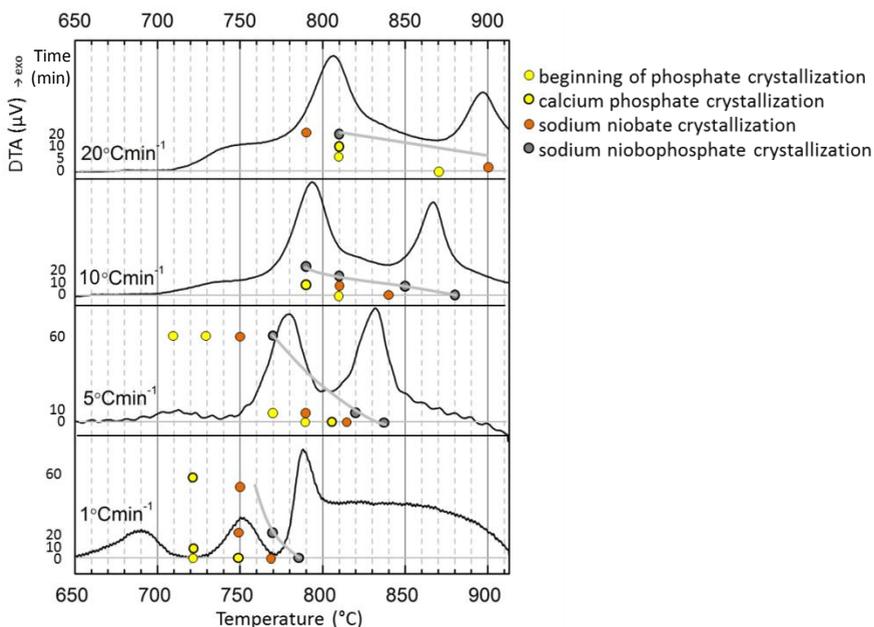


Fig.5. Formation of crystalline phase formation dependence on heat treatment (heating rate, maximum temperature and temperature retention time). Grey line is a guideline for eye to mark slope of time lag-crystalline phase function

By keeping maximum temperature for a longer time, it is possible to crystallize phases that correspond to higher temperatures. At lower heating rate, the time lag that is necessary for high-temperature phases is longer. Technologically crystallization is more controllable in a slow heating process, while the rapid heating rate is more economical.

Crystalline phases. Example of XRD data showing development of crystalline phases during crystallization process are displayed in Fig.6. In all heating modes the phases are formed in the same order:

- In low temperatures calcium phosphates are formed— $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$, $\text{Ca}_2\text{P}_2\text{O}_7$ (monoclinic),
- Afterwards crystallises metastable sodium niobate phase (NaNbO_3 or Nb_2O_5),
- In highest temperatures, the crystalline content is rapidly increased and above mentioned phases recrystallize and forms $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$ and $\text{Ca}_2\text{P}_2\text{O}_7$ (high-temperature tetragonal form); with increase of $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$ content, NaNbO_3 un Nb_2O_5 decreases.

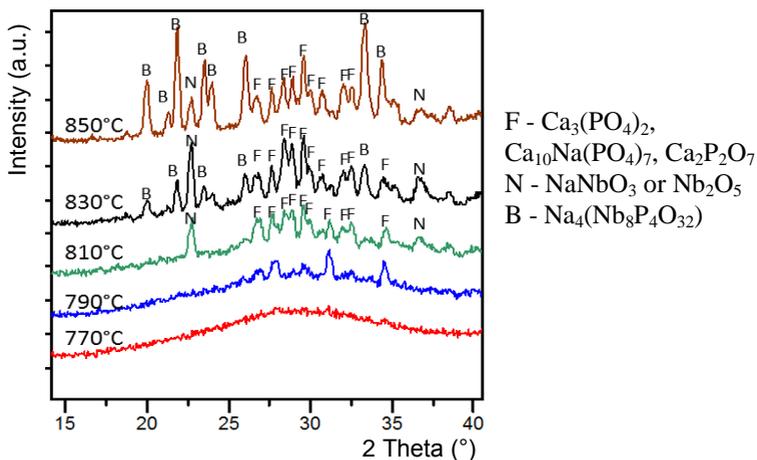


Fig.6. Diffractograms of 8N samples.
Crystalline phase development by heating at 5°C min^{-1}

Microstructure analysis. As it is shown in Fig.7, microstructure varies with heating rate. By SEM-EDS it was detected that the darkest crystals are calcium sodium phosphates, brighter one contains niobium.

At lower heating rate (1°Cmin^{-1}) needle shaped phosphate crystals form, at higher heating rate crystals are more bulky. Classical crystal morphology theory describes that faster crystal growth results in needle shaped or even dendritic crystals. Here in glass crystallization the driving force for crystallization is

temperature, in agreement with previously described experimental data higher crystallization rates are at higher temperatures. But the distinction of crystallization in solution glass has high viscosity at low temperatures (i.e. low heating rate), so only crystals edges grow and diffusion to faces does not happen.

Crystals of NaNbO_3 or Nb_2O_5 are the brightest spots in SEM micrographs. Crystallization of $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$ cannot be directly seen – crystallization takes place at the rest of volume, there are no formation of certain form of crystals.

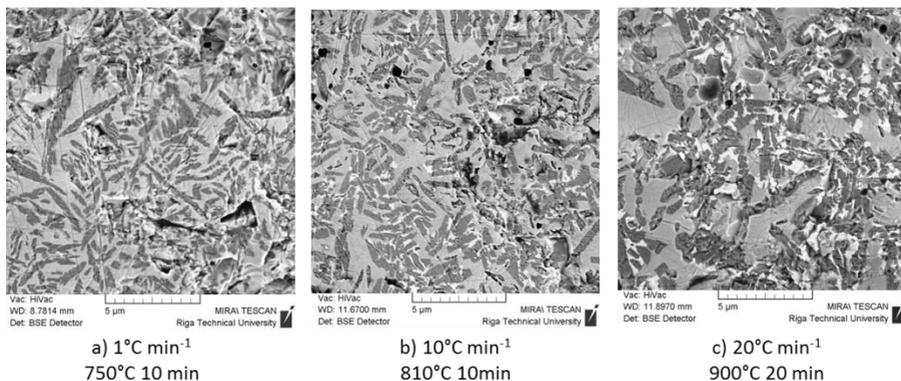


Fig.7. Microstructure of glass-ceramic with crystalline calcium phosphates and sodium niobate obtained by various heating rate. SEM-BSE micrograph

3. Glasses with proportionally changed composition

To evaluate the effect on crystallization process of each of oxides, the 8N composition was varied. The amount of each oxide was changed by 5 mol%.

Decreasing P_2O_5 amount till 27 mol% melt crystallized during cooling – the glass forming ability has significantly decreased. Decreasing Nb_2O_5 amount till 5 mol% melt crystallized from volume and glass forming ability has decreased.

Crystalline phases obtained during slow cooling (C series) and glass reheating till total crystallization (R series) was compared. In C series more and various niobophosphates formed, in R series more calcium phosphates forms. It can be explained as follows: during reheating first forms thermodynamically favourable compound – at low temperatures it is calcium phosphate, but during cooling dominates crystallization of niobophosphates that is kinetically favourable.

Summary of crystalline phases in R series samples as function of Ca/P and Nb/P in parent glass is shown in Fig.8. It can be noticed that the phosphate ratio in niobophosphates depends on calcium amount. As said before during heating first crystallizes calcium phosphates and niobates crystallizes from residual glass

matrix. Thus more calcium in parent glass causes less phosphate in residual glass after crystallization of calcium phosphate.

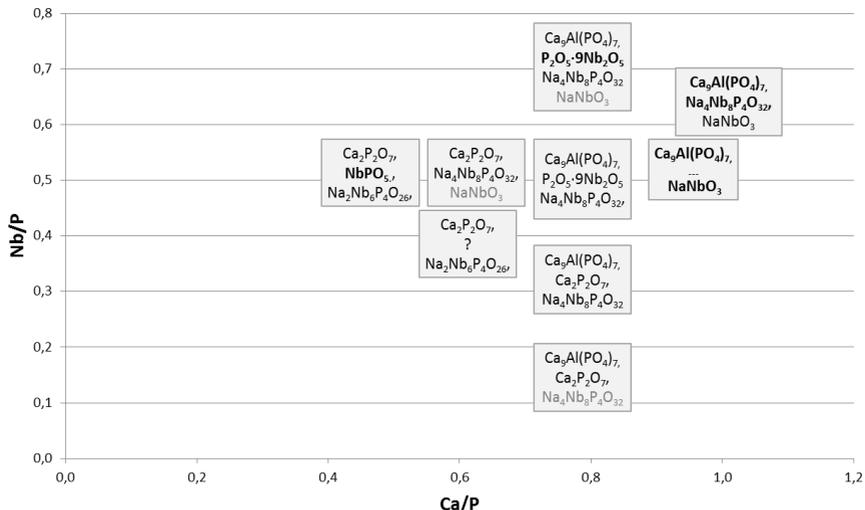


Fig.8. Crystalline phases in as function of Ca/P and Nb/P amounts in parent glass. Bolded fonts – larger amount of phase, lighter fonts – smaller amount

Microstructure. Microstructure for all samples is quite heterogeneous (Fig.9) – there are areas in which the crystallite size is considerably larger than the average. Samples with smaller amount of phosphates have greater amplitude of grain size, but average small grained areas are more homogeneous. Sample with smallest amount of phosphate (27% P_2O_5) was not well sintered.

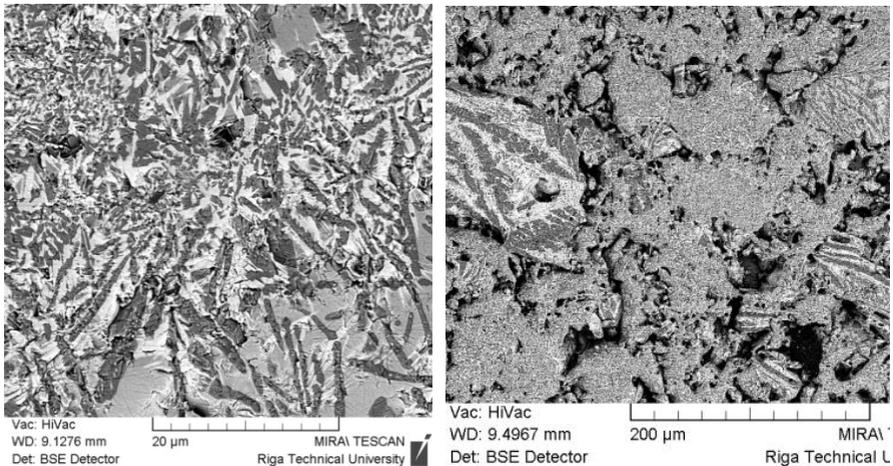
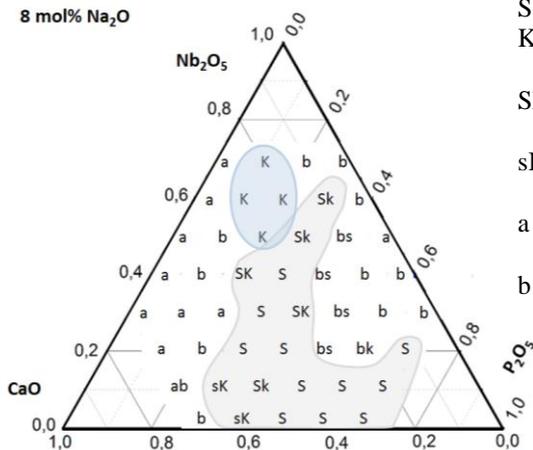


Fig.9. Microstructures of samples with lowered calcium amount and sample with lowered phosphate amount. SEM-BSE micrographs

4. System $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-8Na}_2\text{O}$

To investigate the regularities of crystalline phases formed in the glass-ceramic the whole $\text{CaO-Nb}_2\text{O}_5\text{-P}_2\text{O}_5\text{-8Na}_2\text{O}$ system was investigated. Melting temperature was 1300°C , time of homogenization – 30 min. Firstly glass forming ability was evaluated. The summary is shown in Fig.10.



- S – glass;
- K – glass during cooling completely crystallized;
- Sk – glass during cooling slightly crystallized,
- sK – glass during cooling mostly crystallized;
- a – batch has not melted (loosely sintered powder);
- b – batch has partly melted (well sintered powder)

Fig.10. Glass forming range and a description of crystallinity of samples after melting

Glass forming range is at 30 mol% P_2O_5 and various niobia content and at 10 mol% Nb_2O_5 and various phosphate content.

The photographs of cooled melts according to composition are shown in Fig.11. For glasses with 30 mol% P_2O_5 niobium gives yellow to brownish colour, depending on the amount (10-60 mol%), indicating a higher oxidation state Nb^{5+} . Glass with 10 mol% Nb_2O_5 and increasing the amount of P_2O_5 becomes dark blue, indicating the presence of Nb^{4+} in the structure due to phosphate reductive effect.

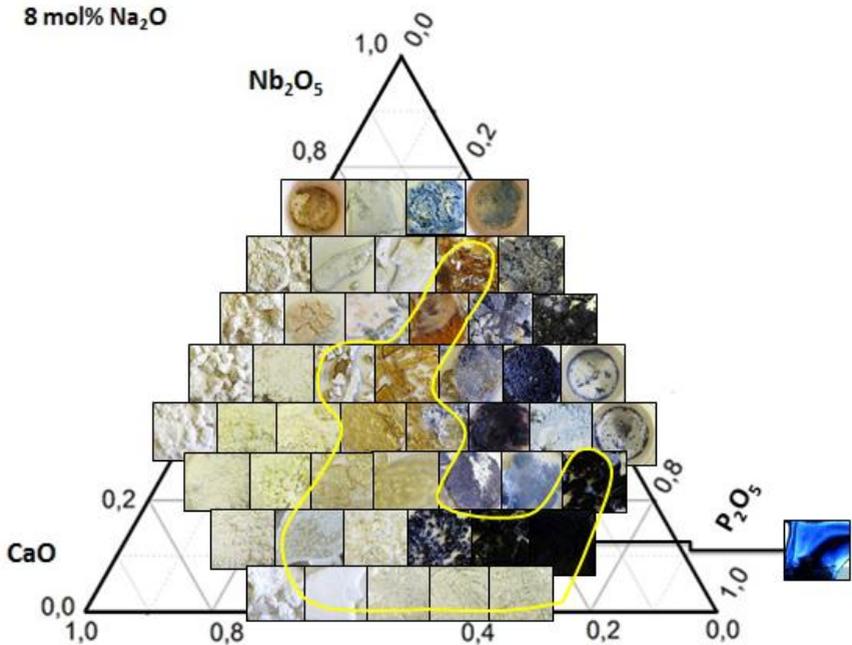


Fig.11. Photographs of cooled melts according to composition. With yellow line the range of glasses is surrounded

In electron dispersive spectroscopy (EDS) analysis it was verified that composition of all obtained glasses are as proportional to that before melting, but there are $0,7 \pm 1,0\%$ till $6,7 \pm 0,2\%$ of aluminum impurity. Alumina source is crucible. More alumina is in glasses with higher amount of calcium. Probably shorter glass chain (more modifier) makes melt more corrosive.

With increasing amount of niobium glass transition temperature increased (Fig.12) – this indicates that niobium has involved in glass network as glass former. Glass stability decreases with increasing amount of niobia.

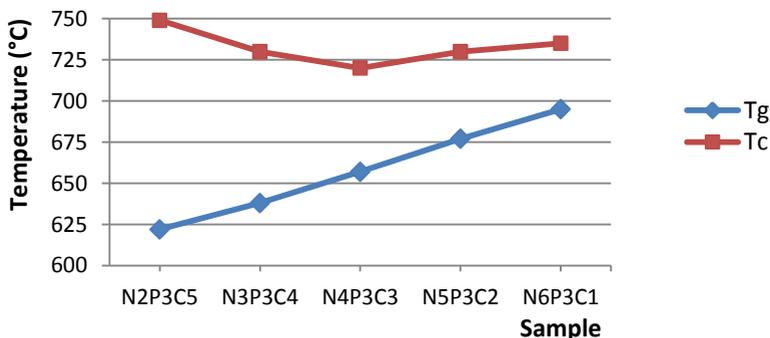


Fig.12. Glass transition temperature (T_g) and lower crystallization temperature (T_c) as a function of composition. N..P..C.. – the amount of Nb_2O_5 , P_2O_5 and CaO respectively (x 10 mol%).

4.1 Crystalline phases formed during cooling

The summary of crystalline phases formed during melt cooling is shown in a Fig.13. There are calcium phosphates forming at the phosphate poor area – where P_2O_5 is less than 30 mol% and niobophosphates at the calcium poor area – where CaO is than 30 mol% and less. Niobium is virtually in all crystalline phases if parent glass contains niobium.

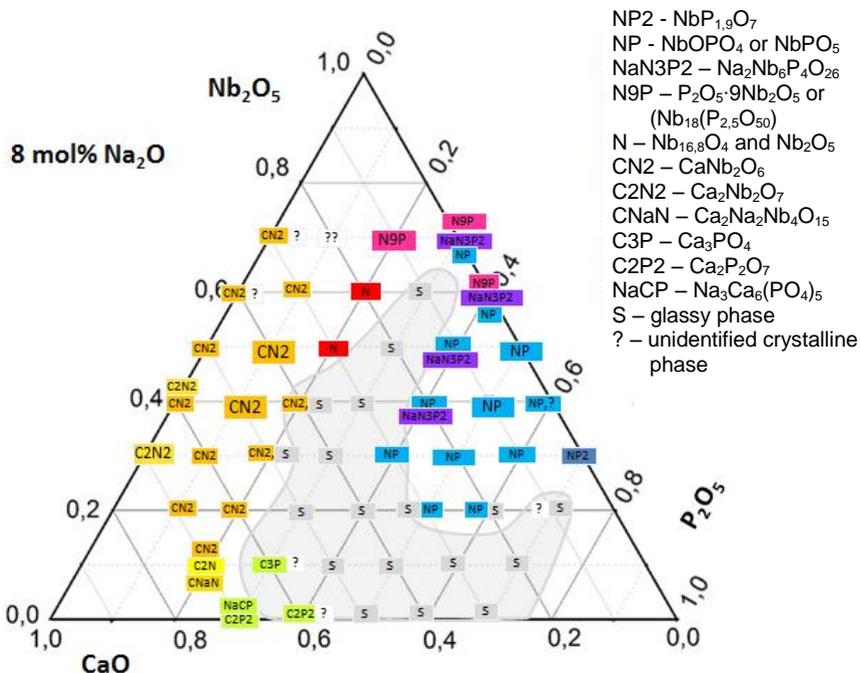


Fig.13. Crystalline phases after melt cooling. Summarized XRD results

4.2 Crystalline phases formed during reheating

In a Fig.14 the summary of crystalline phases formed during reheating till complete crystallization are shown. The phase diagram can be divided in five overlapping regions according to obtained crystalline phases: CaNb_2O_6 , $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$, $\text{Na}_2\text{Nb}_6\text{P}_4\text{O}_{26}$, NbPO_5 and $\text{Ca}_2\text{P}_2\text{O}_7$. All samples have crystalline phases containing niobium on contrary calcium, phosphorous and sodium. There is niobium in crystalline phases of all samples containing niobia.

The similarities in crystalline phase composition are correlating to amount of phosphorus in a sample. Calcium phosphates are forming only in compositions with small niobium content where niobia/phosphate ratio is 6/4 and CaO at least 30 mol%.

NP - NbOPO_4 or NbPO_5
 NaNP - $\text{NaNb}(\text{PO}_4)_3$?
 NaN3P2 - $\text{Na}_2\text{Nb}_6\text{P}_4\text{O}_{26}$
 NaN2P - $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$
 N9P - $\text{P}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$ or
 $(\text{Nb}_{18}(\text{P}_{2,5}\text{O}_{50}))$
 N - $\text{Nb}_{16,8}\text{O}_4$ and Nb_2O_5
 NaN3 - NaNb_3O_8
 NaN - NaNbO_3
 CN2 - CaNb_2O_6
 C3N2 - $\text{Ca}_3\text{Nb}_2\text{O}_8$
 C10NaP7 - $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$
 C3P - Ca_3PO_4
 C2P2 - $\text{Ca}_2\text{P}_2\text{O}_7$
 CaCP - $\text{Na}_3\text{Ca}_6(\text{PO}_4)_5$
 ? - unidentified
 crystalline phase

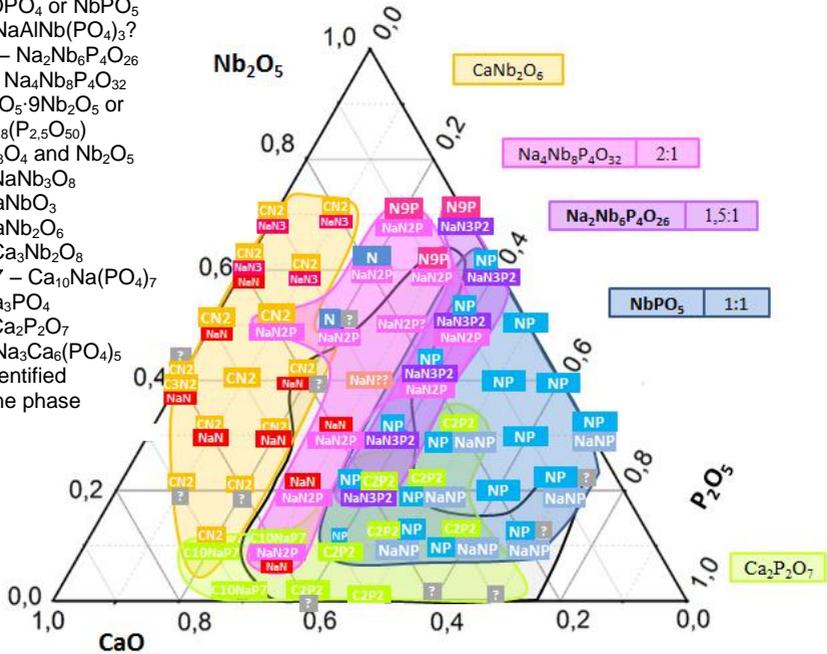


Fig.14. Crystalline phases after reheating. Summarized XRD results

5. Properties of 8N glass-ceramic

Microhardness. 8N glass-ceramic microhardness is $\sim 5,6$ GPa, while other phosphate glasses and glass-ceramic has only 4,5 GPa.

Chemical durability. 8N glass and glass-ceramic is insoluble in water and bases (Fig. 15). In acidic solution calcium phosphates dissolve forming open pore channels instead, that could promote cell integration on material. Amorphous 8N (in Fig. 15 8N-a) is almost insoluble – in boiling HCl after 3h only 4% mass loses. Semi-crystalline and completely crystalline material (in Fig. 15 8N-f and 8N-n) has mass loss approx. 20%, after dissolution open porosity has increased also approx. 20%. After 1 and 5 days in citric acid at 37°C mass loss is only 5 and 10 % respectively.

It can be concluded that semi-crystalline and completely crystalline 8N could be more prospective as biomaterial for bone tissue replacement, because they are more soluble and during dissolution release calcium and phosphate ions and increases porosity.

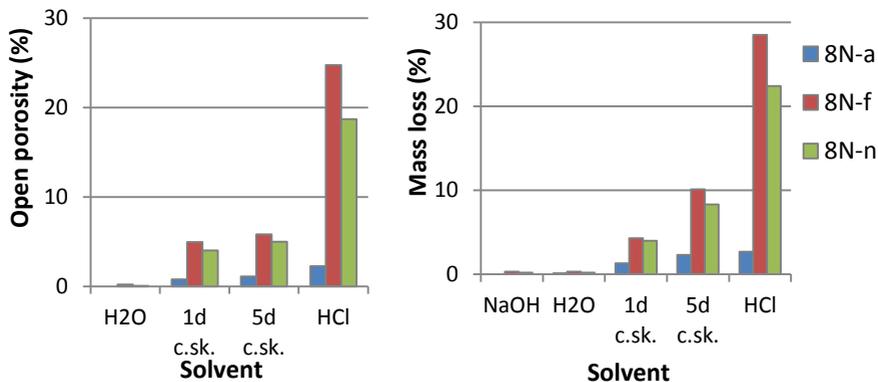


Fig.15. Open porosity and mass loss after treatment in several solvents. 8N-a – amorphous, 8N-f – semi-crystalline, 8N-n – completely crystalline sample

Solubility kinetic. Solubility kinetics in 1M HCl at room temperature is shown in Fig.16. It can be concluded that phosphate phase is almost completely interconnected. After 72 h all the phosphates are dissolved, remaining niobophosphates are practically insoluble.

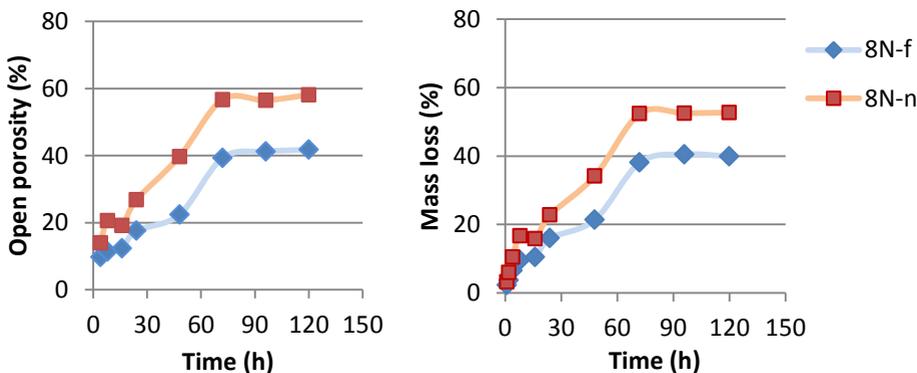


Fig.16. Dissolution kinetics as increase of open porosity and mass loss in 1M HCl. 8N-f – semi-crystalline, 8N-n – completely crystalline sample

In vitro and in vivo tests. 8N glass and glass-ceramic is biocompatible: after 72h tests human osteosarcoma cells MG63-GFP on samples proliferate 2.4 times better than on a control plate, cells are oval to spindle-shaped. That confirms biocompatibility of 8N material.

Contamination limits for bacteria *P.aeruginosa* and *S. epidermidis* are 10^2 CFU/ml. More microorganisms were found on rougher sample 8N-n.

S. epidermidis does not grow on a material after implantation for a 2 and 4 weeks in a rabbit soft tissue. Results were similar for samples contaminated with 10^2 CFU/ml and 10^3 CFU/ml. Higher inflammation effect was in tissue contaminated with *P.aeruginosa*.

CONCLUSIONS

1. For the first time systematical investigation of crystallization process of a $\text{Na}_2\text{O}-\text{CaO}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$ glass system was performed. The crystallization mechanism and regularities in the formation of crystalline phases and the influencing parameters were determined.
2. **The crystallization of niobium-containing compounds.** Niobium-containing compounds are crystallizing at every investigated point of $\text{Na}_2\text{O}-\text{CaO}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$ glass system. Decrease in the amount of calcium and increase in phosphate in parent glass composition increases Nb/P ratio in crystalline phase $-\text{Na}_2\text{Nb}_6\text{P}_4\text{O}_{26}$ and NbPO_5 forms where Nb/P ratio is 3/2 and 1/1 instead of $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$, where the ratio is 2/1. If the content of P_2O_5 is decreased till 30 mol% NaNbO_3 and niobium oxides crystallizes.
3. **The crystallization of calcium-containing compounds.** The main crystalline phases of the system $\text{Na}_2\text{O}-\text{CaO}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$ are CaNb_2O_6 , $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$, $\text{Na}_2\text{Nb}_6\text{P}_4\text{O}_{26}$, NbPO_5 and $\text{Ca}_2\text{P}_2\text{O}_7$. Calcium niobate forms only in a range where content of P_2O_5 is decreased till 20 mol% or less. Calcium phosphates do not crystallize during slow cooling of melt but only in a case of reheating of glass and only in compositions containing less than 30 mol% Nb_2O_5 .
4. **Nb_2O_5 role in glass structure.** By reducing the amount of Nb_2O_5 till 5 mol%, it becomes a modifier and the glass crystallization type changes to volume crystallization. For glasses with 30 mol% P_2O_5 niobium gives yellow to brownish colour, depending on the amount (10-60 mol%), indicating a higher oxidation state Nb^{5+} . Glass with 10 mol% Nb_2O_5 and at least 50 mol% P_2O_5 are dark blue, indicating the presence of Nb^{4+} in the structure due to reductive effect of phosphate.
5. **Crystallization mechanism of 8N glass.** The primary crystalline phases are calcium phosphates ($\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$, $\text{Ca}_2\text{P}_2\text{O}_7$ (monoclinic) and the crystallization starts form surface. Secondary crystalline phases Nb_2O_5 , $\text{Na}_4(\text{Nb}_8\text{P}_4\text{O}_{32})$ un $\text{Ca}_2\text{P}_2\text{O}_7$ (tetragonal) are formed by volume crystallization. Phase transition temperature is significantly dependent on the heating rate, but the heating rate does not affect the composition of phases and their sequence. At faster heating rate increases the role of maximum temperature time lag. Slower heating promotes formation of elongated crystallites.

6. **Solubility of 8N glass and glass-ceramic.** 8N glass and glass-ceramic are virtually insoluble in water and alkali but are soluble in acids. 8N glass-ceramic phases can be arranged according to the solubility in the following sequence (starting from the most soluble), $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$ (monoclinic), $\text{Ca}_2\text{P}_2\text{O}_7$ (tetragonal). Amorphous phase, Nb_2O_5 and $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$ are considered to be poorly soluble. Dissolution of calcium phosphates forms open porosity till 57 vol%.
7. By controlled crystallization of 8N glass various degrees of crystallinity of glass-ceramics may be obtained, that show excellent biocompatibility in ***in vitro and in vivo studies***: osteoblast cells proliferate on the material 2.5 times better than in the control box, the amount of material contamination by bacteria *P. aeruginosa* and *S. epidermidis* is at least 10^2 CFU/ml. *S. epidermidis* does not grow onto 8N glass-ceramic in a rabbit soft tissue. 8N hardness is higher than other phosphate glasses and glass-ceramic.

List of publications on the topic of the thesis

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