ESRF	**Experiment title:** Investigation of kinetics of the crystalline phase growth at the interface of bioactive glasses with simulating body fluid by GID.	**Experiment number**: SC-4123
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Report:

Bioactive glasses (BGs) are a new class of composite materials having open prospects of using in medicine due to their antimicrobial, anti-inflammatory and other properties. It is established fact that BGs stimulate functioning of the bone cells, which leads to the formation of new bone tissue and accelerate the process of regeneration. Therefore BGs are more and more employed in arthroplasty, stomatology, maxillofacial surgery and cosmetology. the experimental aim was to determine the kinetics of growth of crystalline phases of hydroxyapatite (HCAp) on the BG surface, structural changes occurring with glass as a result of exposure in simulating body fluid (SBF), depending on the time of exposure of samples in it and on the chemical composition of glass. Our goal was stepwise study of fundamental process of HCAp layer formation on BG surface to understand an initial reason of HCAp formation and to create new BG with superior properties for implantation in the future.

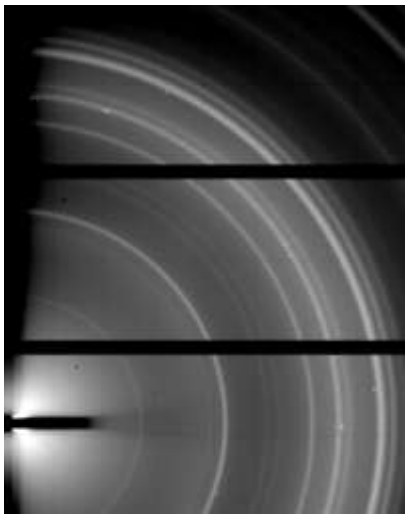
The experiment was carried out using the grazing incidence X-ray diffraction (GID) method at liquid-solid interface in order to determine a mechanism of growing of crystalline phases on bioactive glasses. We have used beam energy 22 keV and 2D detector Pilatus 300K. We have investigated two types of BG: a) $SrO\text{-}B_2O_3\text{-}SiO_2$ with 35-50 mol. % of SrO (sample series № 53, 61 and 66); and b) $Na_2O\text{-}K_2O\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ with ZrO_2, P_2O_5,TiO_2 and F_2 additives (sample series № 1-4). All BG samples are listed in Table 1 with there initial component. Samples of each type were exposed with an appropriate SBF prior the X-ray experiments. Controlling the exposure time we can obtain the samples at stages 1-5 of the bio-chemical reaction (listed above) just before installing them in the X-ray beam. During the experiment we have studied our samples in three conditions: (1) ex situ investigation of bio-glasses with grown HCAp and in situ grows of HCAp on the (2) polished glasses and (3) glass powder into SBF solution.

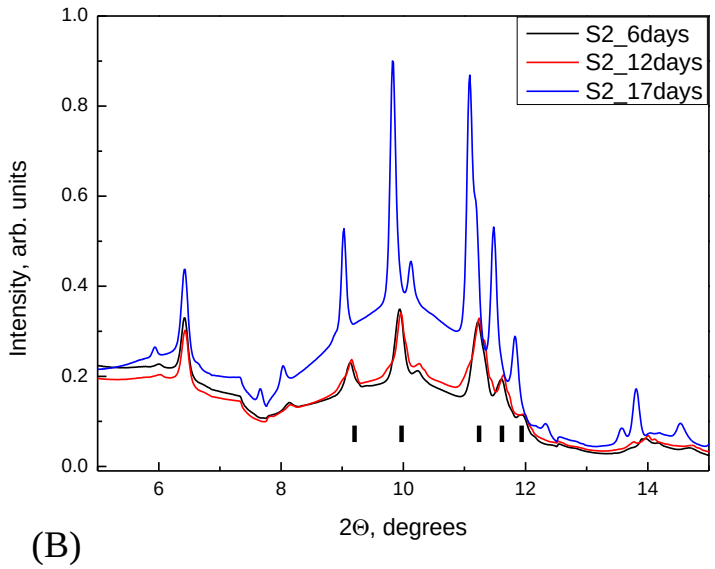
Ex situ mesurements were performed on the each compounds with grown HCAp on the polished glasses surface after 6, 12 and 17 days of maceration of the glasses in SBF solution. Diffraction patterns in GID were obtained on the solid-air interfaces. It was found

that the grown stratum of HCAp after few days of maceration in SBF has polycrystall structure and appears as barely noticeable diffraction rings with the distinct diffraction spots from the separate cristallites. Typical of HCAp peaks are at reflection angles 11.51 deg. for the plane (211) and (121) (intensity 99%), 11.65 deg. for the plane (112) (49% intensity) and 11.91 deg. for the plane (300) for $\lambda = 0.56$ angstroms. Common low value on intencity from the grown layer alows to resolve the most intensive peaks from HCAp. Moreover aditional peaks from another formed structures were revealed, Fig 1

Table 1. A list of initial BG samples with containing components.

№ glass	Components, wt. %										
	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	P_2O_5	TiO_2	F_2	ZrO_2	SrO	B_2O_3
1	68.88	8.22	4.71	13.95	4.24						
2	68.17	8.6	4.66	13.72	3.67				1.18		
3	59.35	6.31	4.61	10.62	9.29	1.31	5.77	2.72			
4	58.66	6.45	4.82	11.21	8.83	1.08	5.5	3.45			
53	35									40	45
61	27.5									45	27.5
66	32.5									35	32.5





(A) (B)

Fig.1 – (A) An expemple of the diffraction picture from the air-solid interface of the grown HCAp of the sample S4 after 17 days in SBF. (B) Diffraction intensity after 6, 12 and 17 days of maceration of the glasses S2 in the SBF.

During the in situ experiment the polished bio-glass have been dipped in SBF into the liquid cell with permanent controled temperature T = 37°C. After the short alignment of the samples we started timescan for 6 houses. As a result we wanted to study the first spets of the nucleation and growth process of HCAp phase by GID. The data analizis have been confirmed the emergence of HCAp in small quantaty during the first hours, but the general picture of the investigation process failed to detect for next reasons:

1) Small nucleated HCAp phase gives a small intensity value on the background of the SBF solution, glass, capton cell windows and air at the diffraction pattern. This allows to indentify only the most intense peaks of the new formed phase that complicates the subsequent analysis.

2) Analysis of the most intense peaks evolution from HCAp during the few hours of X-ray irradiation revealed the influence of radiation damage in the analized phase. It is

manifested in form of decreasing of the peaks intensity after the displacement of the beam on new position during the experiment, see Fig. 2.

3) The analysis of the HCAp is hampered by the presence of additional peaks. It can be correlated with others chemical compounds which is formed during the HCAp synthesis: $Ca(H_2PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$, $Ca_{10} \cdot (PO_4)_6 \cdot (OH)_2$, $Ca_4H(PO_4)_3 \cdot 5H_2O$, $Ca_3 \cdot (PO_4)_2$,$Ca_2 \cdot P_2O_7 \cdot 2H_2O$, SiO_2, NaCl, $NaHCO_3$, KCl, $K_2 \cdot HPO_4$, $MgCl_2$, $CaCl_2$, $Na_2 \cdot SO_4$, $NH_2 \cdot C(CH_2 \cdot OH)_3$.

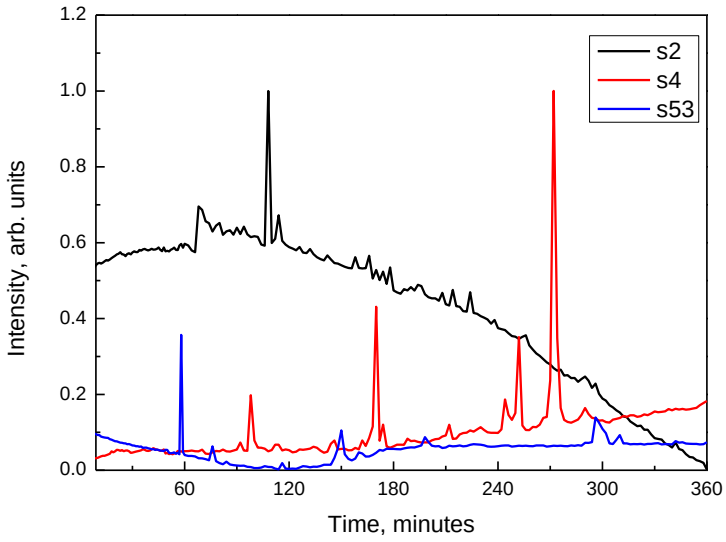


Fig. 2 – Temporary evolution of the most intence HCAp peak (300) during the in situ experiment for the bioactiv glass samples S2, S4 a and S53.

The data from powder glass samples in SBF also demonstrates the formation of small quantity of HCAp crystalines and low signal at the diffraction patterns.

Thus we have been demonstrated a possibility to registrate the appearance and grows of the HCAp phase on the surface of bioactive glasses during the in situ experiment, but their quantity is not enough for the description of the dynamics of the investigated process. For the successful continue of this topic we plane to modify this in situ experiment by such ways as a using of microbalance sample cell, increesing of the porosity and surface of the glass and etc.