

## STRUCTURAL BEHAVIOUR OF NIOBIUM PHOSPHATE VITROCERAMICS IN SIMULATED BODY FLUID

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The changes induced on the local structure of calcium-phosphate vitroceramics with  $\text{LiNbO}_3$  crystallites by increasing of  $\text{Nb}_2\text{O}_5\text{-Li}_2\text{O}$  content in the precursor glass sample as well as by soaking in simulated body fluid (SBF) were investigated by  $^{31}\text{P}$  nuclear magnetic resonance. The  $^{31}\text{P}$  magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra of these samples consist in two groups of lines occurring between  $-7$  and  $-10$  ppm respectively  $-23$  and  $-34$  ppm. The preponderance of the  $^{31}\text{P}$  resonant lines recorded between  $-7$  and  $-10$  ppm increases with  $\text{Nb}_2\text{O}_5\text{-Li}_2\text{O}$  content. On the other hand, the MAS NMR data evidence that the atomic environment of phosphorus atoms in the second configuration sphere, particularly when calcium is the main neighbour, is modified after immersion in SBF.

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### 1. Introduction

Phosphate glasses and ceramics are both of technological interest for electrochemistry devices, electronic industry and of medical interest as bioactive materials [1, 2]. The phosphate glass network is dominated by a pattern of the linkage between the  $\text{PO}_4$  tetrahedra. The addition of other oxides leads to a depolymerisation of the network corresponding to breaking of P-O-P links and converting of bridging oxygens to non-bridging oxygens [3]. Phosphate glass-ceramics containing ferroelectric niobate crystallites could be useful for electromagnetic therapy.

The bioactive glasses are widely investigated due to their successful use in various clinical applications. The unique feature of bioactive glasses is their chemical and biological activity when exposed to human fluids [4]. Vitroceramic samples with ferroelectric niobate crystallites could be useful for electromagnetic therapy. Due to its high resolution and sensitivity the nuclear magnetic resonance spectroscopy is a adequate tool for local structure characterisation [5].

This study is focussed on the investigation of the local structure around phosphorus atoms in calcium phosphate glass-ceramics by progressive addition of  $\text{Nb}_2\text{O}_5\text{-Li}_2\text{O}$  before and after soaking of samples in simulated body fluid (SBF) by means of solid-state magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy.

### 2. Experimental

The precursor glasses belong to  $(100-x)[\text{CaO}\cdot\text{P}_2\text{O}_5]_x(\text{Nb}_2\text{O}_5\text{-Li}_2\text{O})$  system, with  $x = 1, 5, 10$  and  $20$  mol %. The glass samples were prepared using as starting materials reagent grade  $\text{Nb}_2\text{O}_5$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The homogenised mixtures were melted at  $1200$  °C for 10 minutes and quickly undercooled at room temperature. Glass transition and crystallization temperatures were determined by differential thermal analysis [6] and according to these data the glass samples were partially crystallised by heat treatment applied at  $650$  °C for 100 hours. The crystalline phases identified by X-ray diffraction are  $\text{LiNbO}_3$  and different crystalline phases containing phosphorus. The obtained vitroceramic samples were soaked for 72 hours in SBF solution [7] containing  $\text{NaCl}$ ,  $\text{NaHCO}_3$ ,  $\text{KCl}$ ,  $\text{K}_2\text{HPO}_4\cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ,  $1\text{N-HCl}$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$ .

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MAS NMR spectra were collected at Larmor frequency of 161.9 MHz for  $^{31}\text{P}$  using a full digital BRUKER Avance 400 UltraShield<sup>TM</sup> spectrometer, with superconductor magnet of 9.4 T. Solid-state NMR inversion recovery 1-D experiments were performed using a standard bore probe head with 4 mm diameter rotor and spinning speed at magic angle of 12 kHz. All  $^{31}\text{P}$  NMR chemical shifts were expressed in ppm relative to a 85%  $\text{H}_3\text{PO}_4$  water solution. NMR measurements at room temperature were carried out before and after samples soaking in SBF.

Inversion recovery sequence spectra were acquired at 12 kHz spinning rate using a pulse sequence described in Fig. 1. A  $t1ir1d$  sequence with a recycle delay of 100 seconds was used to prevent saturation and a second delay between  $\pi$  and  $\pi/2$  pulses of 0.5 second to obtain high transversal magnetisation. A number of 32 or 64 scans was acquired. All spectra were processed using Bruker NMR programs and then they were simulated using Dmfit program [8].

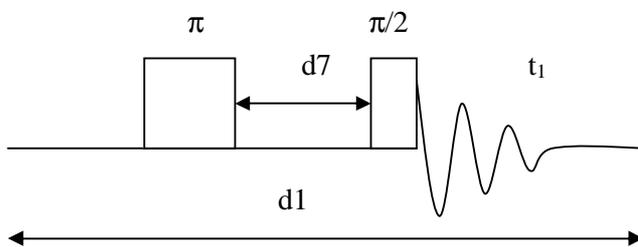


Fig. 1. Inversion Recovery “t1ir1d” pulse sequence.

### 3. Results and discussion

Fig. 2 illustrates the evolution of  $^{31}\text{P}$   $t1ir1d$  1-D MAS NMR spectra of the  $(100-x)[\text{CaO}\cdot\text{P}_2\text{O}_5]x(\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O})$  glass-ceramics as a function of  $\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O}$  content over the range from 1 to 20 mol %. The spectra exhibit complete resolved isotropic resonances grouped in two distinct ranges, one group of four resonances at small chemical shifts (between  $-7$  ppm and  $-10$  ppm) and a second one between  $-23$  ppm and  $-34$  ppm. In Table 1 are given the measured and simulated chemical shifts and linewidths (full width at the half maximum) for the sample with  $x = 5$  before SBF soaking. The shape of all signals is narrow and symmetric, typically for cubic structures. This kind of structure [9] is confirmed once more by spin-lattice relaxation time ( $T_1$ ), which for all the samples is around 650 seconds.

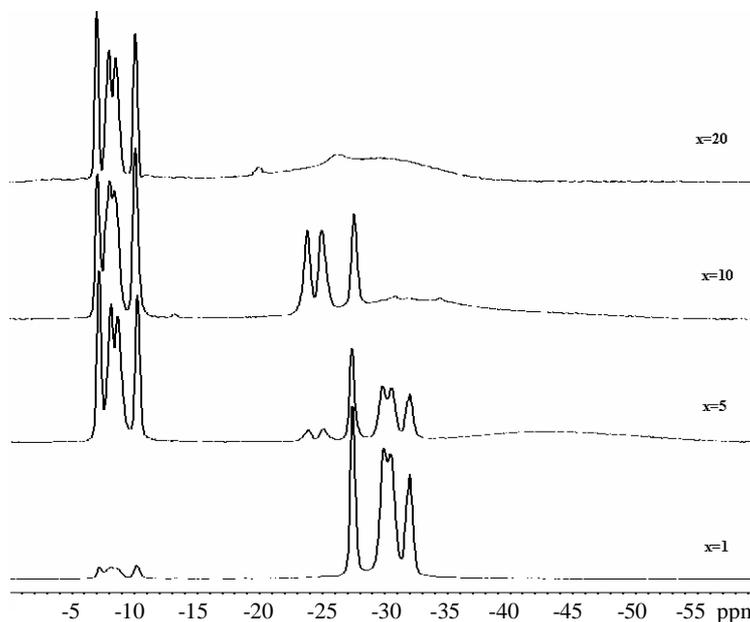


Fig. 2.  $^{31}\text{P}$   $t1ir1d$  MAS NMR spectra of  $(100-x)[\text{CaO}\cdot\text{P}_2\text{O}_5]x(\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O})$  vitroc ceramics before soaking in SBF.

The structure of phosphate glasses can be described very similar to that of silicate glasses in terms of four individual  $Q^n$  sites, where  $n$  is the number of bridging oxygens in a  $PO_4$  group. Pure vitreous  $P_2O_5$  consists in a polymeric structure of  $PO_4$  units. The presence of the modifier like alkali decreases the number of bridging oxygens (P-O-P bridge) in  $PO_4$  units, while its negative charge increases [10].

In the first coordination sphere all the P neighbors are O atoms. The differences appear in the second coordination sphere, where the O atoms can be bound with different atoms. Another reason of different of  $^{31}P$  resonant frequency is the bond lengths and angles. The distortion from the cubic structure is smaller for the site with lower chemical shift.

Table 1. Measured and simulated chemical shift  $\delta_{iso}$  and linewidth  $\Delta\nu_{1/2}$  for  $5[Nb_2O_5 \cdot Li_2O]95[CaO \cdot P_2O_5]$  sample.

Position $^{31}P$	Measured		Simulated	
	$\delta_{iso}$ (ppm)	$\Delta\nu_{1/2}$ (ppm)	$\delta_{iso}$ (ppm)	$\Delta\nu_{1/2}$ (ppm)
1	-7.037	0.42	-7.060	0.41
2	-8.026	-	-7.950	0.53
3	-8.544	-	-8.600	0.71
4	-10.146	0.48	-10.140	0.44
5	-23.758	0.60	-23.760	0.59
6	-25.030	0.65	-25.020	0.64
7	-27.291	0.45	-27.280	0.44
8	-29.740	-	-29.710	0.66
9	-30.400	-	-30.460	0.66
10	-31.954	0.75	-31.900	0.69

In order to observe the structural effect of SBF, all the samples were measured, by using the same third inversion recovery pulse program, after 72 hours of soaking in SBF. The relaxation delay of  $^{31}P$  nucleus for all these samples is really long, around 650 seconds. For measurements we have used 100 seconds recycle delay and 0.5 seconds delay between first pulse ( $\pi$ ) and second pulse ( $\pi/2$ ). To avoid the saturation 5.4 dB power attenuation was used. Fig. 3 points out the changes occurred in  $^{31}P$  MAS NMR spectra after samples treatment with SBF.

For sample with  $x = 1$  one observes an intensity decrease for the signals with chemical shift  $-29.83$  ppm and  $-30.35$  ppm as result of some local structural distortions, implying Ca in the second coordination sphere of P. For the sample with  $x = 5$  one observes a completely different behaviour, the fraction of distorted structures growing for signals with high chemical shift. The intensity increase is not typical only for crystalline structures, this effect also appearing in the noncrystalline structure.

The NMR spectrum of  $90[CaO \cdot P_2O_5]10(Nb_2O_5 \cdot Li_2O)$  sample shows local structure differences especially for the phosphorus sites giving resonances at higher chemical shifts and denotes a distortion of the phosphorus environment surrounded by calcium atoms in the second coordination sphere.

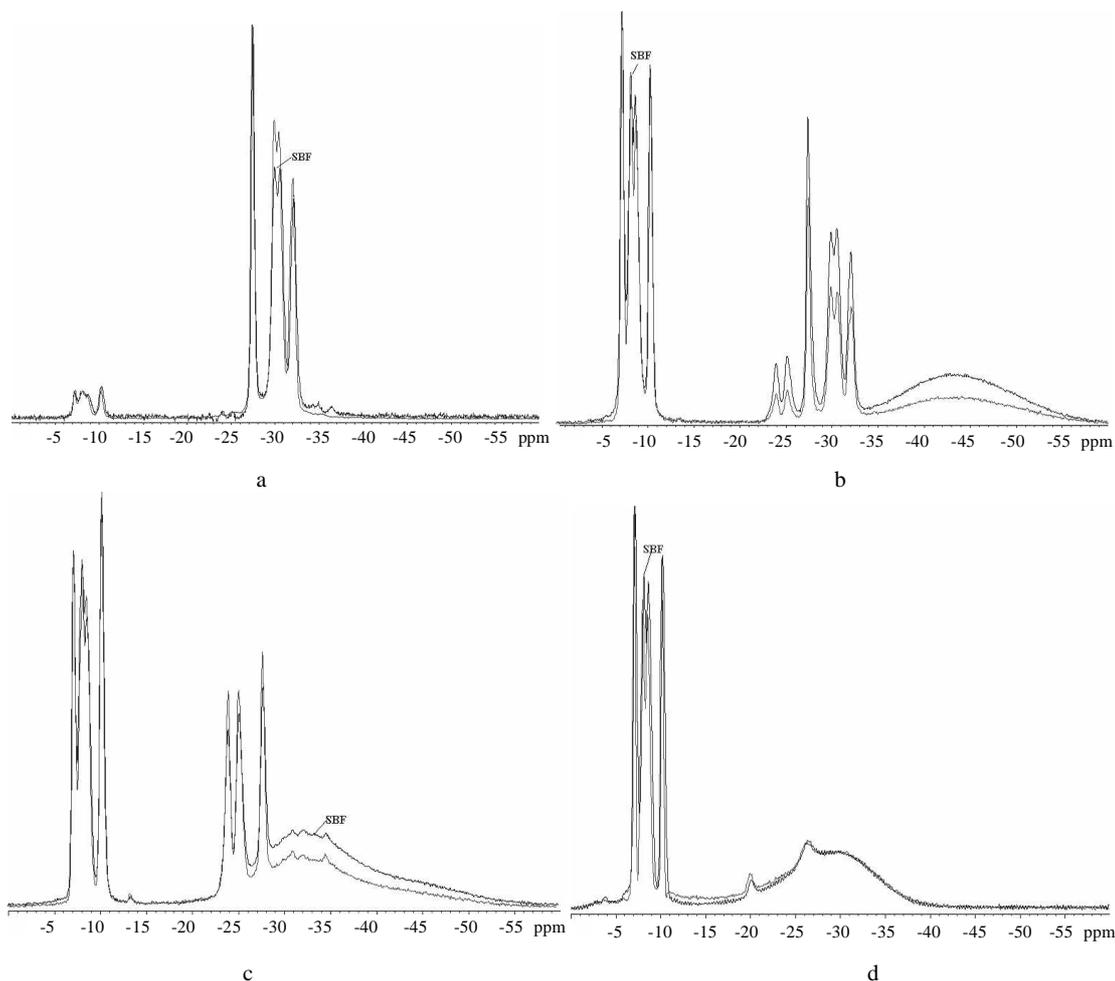


Fig. 3.  $^{31}\text{P}$  NMR MAS spectra before and after SBF soaking of sample with  $x = 1$  (a),  $x = 5$  (b),  $x = 10$  (c) and  $x = 20$  (d).

For  $80[\text{CaO}\cdot\text{P}_2\text{O}_5]20(\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O})$  sample only minor structural changes around phosphorus atoms take place as result of SBF soaking.

The structural changes appeared after immersion of the glass-ceramic samples in SBF are due to the chemical reactions with the SBF and also to the deposition on the samples surface of ions like calcium and phosphorus from the SBF. The results could suggest that the surface of the samples may react different with the SBF because of the different crystalline phases formed after heat treatment of the precursor glass samples.

#### 4. Conclusions

The heat treatment applied on  $(100-x)[\text{CaO}\cdot\text{P}_2\text{O}_5]x(\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O})$  glasses lead to development of  $\text{LiNbO}_3$  and phosphorus containing crystalline phases. Pulse and inversion recovery programs in  $^{31}\text{P}$  MAS NMR were used to investigate the local and intermediate range order around phosphorus in this quaternary glass-ceramic system.  $^{31}\text{P}$  MAS NMR spectra consist of two groups of lines recorded between  $-7$  and  $-10$  ppm respectively  $-23$  and  $-34$  ppm. With increasing  $x$  the four lines between  $-7$  and  $-10$  ppm dominate the NMR spectrum and the group between  $-23$  and  $-34$  ppm emerges in a broad line for  $x = 20$ .

After 72 hours SBF immersion the local structure around the phosphorus atoms is differently changed for various  $\text{Nb}_2\text{O}_5\cdot\text{Li}_2\text{O}$  contents. This implies changes in the second

coordination spheres preponderantly occurring from calcium cations for  $x \leq 10$  as a result of the chemical reactions with the SBF and also of deposition on the samples surface of ions like calcium and phosphorus from the SBF.

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