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Multinuclear Solid State NMR Investigations of Crystallization Processes in Glass Ceramics of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O-CaO-P}_2\text{O}_5\text{-F}$ System

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Abstract. The crystallization of needle-like apatite from a glass ceramic of composition (mole.%) 61.5 SiO_2 -9.4 Al_2O_3 -9.2 Na_2O -7.7 K_2O -6.0 CaO -1.9 P_2O_5 - 2.5 F with minor additional components of CeO_2 , ZrO_2 , TiO_2 , Li_2O and B_2O_3 , was monitored by high-resolution solid state NMR utilizing the magnetic moments of ^1H , ^{19}F , ^{27}Al , and ^{31}P . Systematic studies of bulk and powder samples subjected to well-defined annealing protocols indicate the utility in particular of ^{19}F magic-angle spinning (MAS) NMR to reveal the chemical changes occurring as a function of heating time and temperature. The parent glasses contain multiple fluorine sites, which act as joint reservoirs in the formation of the apatite phase crystallizing at temperatures exceeding 700 °C. The spectra suggest further that small amounts of this phase even form at lower annealing temperature.

Introduction

The development of glass ceramics for useful applications as biological implants requires strict control not only of the chemical composition, but also of shape, morphology, and the mode of interpenetration of the various crystalline and glassy phases involved. Recent work has shown that the formation of needle-like apatite, an important biomaterial, can be controlled by crystallization from a phase-separated glassy precursor [1]. In essence, apatite is precipitated via homogeneous nucleation of a droplet phase within a phase separated glass in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O-CaO-P}_2\text{O}_5\text{-F}$ system. This crystallization process has been studied in detail, using scanning electron microscopy, X-ray powder diffraction and various complementary analytical techniques [2]. In the course of these studies, it was found that apatite crystallization is preceded by the formation of a crystalline precursor phase of composition NaCaPO_4 , and a second, yet unidentified crystalline material. At the present time, it is unclear whether apatite forms via a heterogeneous reaction of the primary NaCaPO_4 crystals with the surrounding glassy matrix or whether the process is rather described by a reaction at the interfaces between the two glassy phases. To elucidate the mechanism in more detail, the use of alternative analytical techniques is essential. In particular, solid state NMR techniques appear promising,

due to their well-proven ability to provide a wealth of structural information on disordered materials and glasses [3]. Issues that remain to be resolved include (1) the distribution of phosphate and fluoride over the two distinct microphases in the glassy precursor material, (2) the local coordination environments around these nuclei, (3) the origin and identity of intermediate phases formed during the crystallization process at various annealing temperatures, and (4) the influence of sample morphology (powder or bulk) on mechanism and product distribution. In the present study we describe the first application of multinuclear high-resolution solid state NMR techniques to this field of study. On the basis of the initial results obtained we will discuss the potential of solid state NMR techniques to provide detailed answers to the above issues.

Experimental.

Glass with the composition (mole.%) 61.5 SiO₂-9.4 Al₂O₃-9.2 Na₂O-7.7 K₂O-6.0 CaO-1.9 P₂O₅- 2.5 F- 0.2 TiO₂-0.3 CeO₂-.0.5 Li₂O-0.3 B₂O₃ was melted at 1480 °C for 1 h and 40 min and cast into monolithic blocks of approximately 1x2x10cm. After cooling the melt the glass blocks were cut into smaller monolithic bodies and their nucleation and crystallization properties were studied by subsequent heat treatment protocols, summarized in Table I. Characterization of the resulting products has been described in detail in reference [2]. ³¹P solid state NMR spectra were collected in the single-pulse mode at 121.5 MHz, using a Bruker CXP-300 spectrometer equipped with a 4mm MAS-NMR probe, providing sample spinning rates near 10 kHz. 400-800 scans were acquired at a repetition time of 10 seconds. Chemical shifts are reported relative to 85% H₃PO₄. ¹H and ¹⁹F MAS-NMR spectra were acquired on a Bruker DSX-500 spectrometer. While the proton spectra were obtained at the corresponding field strength of 11.7 T using a 12kHz rotation speed and 2.5 seconds relaxation delay, we conducted the ¹⁹F NMR studies at 188 MHz in a 4.65 T magnet. In this case, MAS at spinning rates of 5-6 kHz was carried out within 7mm zirconia rotors, and 360 scans were acquired with a relaxation delay of 5 seconds. Experiments using longer relaxation delays (up to 200s) were conducted to ensure that the spectra obtained under the above-reported conditions yielded representative results. The acquisition of both the ¹H and ¹⁹F spectra required the use of the DEPTH pulse sequence [4] designed for the suppression of considerable

probe background signals. As chemical shift references we used tetramethylsilane (TMS) and CFCl_3 for ^1H and ^{19}F , respectively.

212a	glass, no annealing	212e	700°C/8h
212b	400°C/ 15 min	212f	700°C/8h + 1050°C/2h
212c	580°C/15 min	212g	850°C/1h
212d	640°C/15 min	212h	1050°C/1h

Table 1: Sample notation and heat treatment conditions

Results

Table 2 summarizes the ^{31}P , and ^1H NMR chemical shifts of all the samples studied. The ^{31}P NMR spectra are collected in Figure 1. Aside from the parent glass, whose MAS-NMR line is substantially broadened by a distribution of chemical shifts (linewidth 8.3 ppm), all of the annealed samples show spectra that are essentially indistinguishable from each other, and possess a markedly reduced linewidth (3.3 ppm). This isotropic chemical shift value of 3.5 ppm is consistent with that reported for fluoroapatite (FAP) [5]. These results suggest that annealing at 400 °C for 15 min suffices to convert the large majority of the phosphorus atoms into the crystalline state. At higher annealing temperatures no further change in the ^{31}P NMR spectra is apparent.

The ^1H MAS-NMR spectra summarized in Figure 2 show two kinds of signals. The broad peak near 5 ppm is easily assigned to surface-adsorbed water, while the sharp resonances at 0.8 and 1.2 ppm correspond to peaks previously reported for various proton environments in fluoro-hydroxyapatites [6]. Therefore, we assign these resonances to OH^- impurities in FAP. These results indicate that even the parent glass contains such environments, either in the form of highly disordered crystalline domains or as an amorphous precursor phase. Again, no distinct influence of the annealing time or temperature can be noted on the spectra.

Finally, Figure 3 and Table 3 present the ^{19}F MAS-NMR results. Here it is most significant, that the spectra reveal three distinct ^{19}F environments. While the sharp line at -100 ppm signifies the presence of crystalline fluoroapatite [7], the spectra of all of the samples annealed at temperatures below 700 °C indicate that the majority of the fluorine atoms are present in two additional distinct environments,

characterized by chemical shifts near -120 to -130 ppm and -190 ppm, respectively. While the detailed assignment of these resonances to specific fluorine environments is uncertain at the present time, the extremely large linewidths indicate the presence of a very wide chemical shift distribution as is quite typical of glassy materials. Inspection of the ^{19}F solid state NMR chemical shift data base [8] suggests that the chemical shift range of -120 to -130 ppm reflects fluoride ions in the vicinity of the cations Na^+ , K^+ , and/or Ca^{2+} . In contrast, the chemical shift of -190 ppm most likely signifies an interaction with aluminum atoms in the glass matrix. Experiments with variable relaxation delays reveal that the ^{19}F species resonating at -190 ppm is characterized by a significantly larger spin-lattice relaxation time compared to the other two fluorine environments. This result reveals the absence of ^{19}F - ^{19}F spin-diffusion, suggesting that these fluorine species are distributed over two distinct microphases.

Annealing at 700 °C for 8hrs produces a marked change in the spectra. All of the intensity of the broad resonance at -120 to -130 ppm has disappeared, and the intensity of the fluoroapatite signal now is greatly enhanced. As a consequence, the -190 ppm resonance appears „dwarfed“ in the ^{19}F spectra, however, close inspection reveals, that the -190 ppm peak is retained in all of these samples, up the highest annealing temperatures studied.

$\delta(^1\text{H})/\text{ppm}$	assignment	$\delta(^{31}\text{P})/\text{ppm}$	assignment
4.8	surface-adsorbed water (212a)	5.0	PO_4^{3-} (glass)
1.2	OH^- impurities in FAP	3.5	NaCaPO_4 + FAP
0.8	OH^- impurities F^- in FAP		(all other samples)

Table 2: ^1H and ^{31}P chemical shifts observed and assignments.

Figure 1: 121.5 MHz ^{31}P MAS-NMR spectra of the samples under study

Figure 2: 500.1 MHz ^1H DEPTH90-180-180 MAS-NMR spectra of the samples under study. The spectrum on the bottom left is the probe background signal measured under these conditions.

$\delta(^{19}\text{F})/\text{ppm}$	assignment	samples observed
-100	FAP ⁺	212a-h
-120 to -130	F ⁻ (Na, Ca, K) in glassy phase	212a-d
-190	F ⁻ (Al) (second glassy phase)	212a-h

Table 3. ^{19}F NMR chemical shifts observed and assignments.

Figure 3: 188.8 MHz ^{19}F MAS-NMR spectra of the samples under study

Discussion

The NMR results lend support to the crystallization model previously proposed and provide significant additional information. First of all, the ^{19}F and ^1H NMR results clearly show that even the glassy sample, prior to any annealing treatment, contains small amounts of crystalline fluoroapatite or of an disordered precursor phase with the same local environment. This is particularly obvious from the observation of the -100 ppm resonance in the ^{19}F NMR spectra. Most of the fluorine component, however, remains distributed between the two phase-separated glassy domains, giving rise to the broadened resonances at -120 to -130 and -190 ppm, respectively. Short-term annealing within the temperature range 400 - 580 °C (samples 212b-d) leads to crystallization of the entire phosphorus component in the glass, as is clearly indicated by a marked reduction in the ^{31}P NMR linewidth and a shift in the resonance center of gravity from 5 ppm to 3.5 ppm. This finding correlates well with the previous XRD-detection of a sodium calcium phosphate precursor phase in samples annealed at temperatures above 500 °C [2]. In contrast, the ^{19}F NMR spectra reveal that the local environment and the chemical state of the fluoride component remains unaltered by this treatment. Crystal formation involving the majority fluoride component under formation of additional FAP is only detected by treatment at temperatures of 700 °C or higher. However, even under these treatment conditions, residual fluoride (most likely interacting with Al) remains in the amorphous state, giving rise to the signal component at -190 ppm. This result is not unexpected, since the F/P ratio of the batch composition ($2.5/3.8$) is higher than that of FAP ($1/3$), so that not all of the fluoride can end up in the form of fluoroapatite. The dramatic change in the ^{19}F NMR spectra is consistent with the observation of FAP in the XRD at treatment temperatures above 700 °C [2]. We note that the crystallization of FAP does not alter the appearance of the ^{31}P NMR spectrum in any significant way. Based on the other evidences we are forced to conclude that the chemical shift difference between NaCaPO_4 and FAP is not resolved in the ^{31}P MAS-NMR spectra. In principle, this question can be resolved by ^{19}F - ^{31}P double resonance NMR experiments. Finally, both XRD and DSC results suggest the presence of yet another unidentified phase, undergoing a reversible phase transition near 640 °C.

The NMR results, which were obtained on the quenched samples, do not provide any evidence for the involvement of either the phosphorus or the fluoride components of the glass. Ultimate proof for or against their involvement will come from in-situ high-temperature NMR studies, which are currently in progress. In summary, the results of the present study illustrate the power and potential of solid state NMR as a sensitive probe of crystallization processes in bioceramics. The present application to a sample in which both fluoride and phosphate are minor constituents takes particular advantage of the element-selective feature of solid state NMR. Further studies including more advanced experiments are currently in progress.

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References

- [1] Höland, W.; Frank, M.; Schweiger, M.; Rheinberger, V. *Glasstechn. Ber. Glass Sci. Technol.* **C67** (1994), 117.
- [2] Höland, W.; Rheinberger, V.; Frank, M. *J. Noncryst. Solids* **253** (1999), 170-177
- [3] Eckert, H. *Prog. NMR Spectrosc.* **24** (1992), 159-293
- [4] Cory, D. G.; Ritchey, W. M. *J. Magn. Reson.* **80** (1988), 128
- [5] Rothwell, W. P.; Waugh, J. S.; Yesinowski, J. P. *J. Am. Chem. Soc.* **102** (1980), 2637
- [6] Yesinowski, J. P.; Eckert, H. *J. Am. Chem. Soc.* **109** (1987), 6274-6281.
- [7] Braun, M.; Hartmann, P.; Jana, C. *J. Mater. Sci.: Mater. Med.* **6** (1995), 150.
- [8] Miller, J. M. *Prog. NMR Spectrosc.* **28** (1996), 255.