

# <sup>31</sup>P Nuclear Magnetic Resonance and X-Ray Diffraction Studies of Na-Sr-Phosphate Glass-Ceramics

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**Abstract.** A set of Na-Sr-phosphate glass and glass-ceramic samples, with general formula  $x\text{SrO}:(0.55-x)\text{Na}_2\text{O}:0.45\text{P}_2\text{O}_5$ , were prepared and analysed by solid state <sup>31</sup>P nuclear magnetic resonance spectroscopy and X-ray powder diffraction. The results show the presence of  $Q^1$  and  $Q^2$  phosphate species in all samples. At low concentrations of  $\text{Sr}^{2+}$  ( $x \leq 0.20$ ) the strontium is preferentially incorporated in  $\text{Sr}^{2+}\text{-}Q^1$  crystalline phases, and only at higher  $\text{Sr}^{2+}$  concentrations are crystalline phases present which  $\text{Sr}^{2+}$  is associated with  $Q^2$  phosphate units.

## Introduction

Glasses and glass-ceramics are widely used as biomaterials, mainly as bone replacement materials [1] and as base materials for dental restorations [2, 3]. One of the main advantages of phosphate based materials, and particularly the Na-Ca-phosphate system, is their chemical relationship with hydroxylapatite, one of the main constituents of bone and teeth. However, X-ray examination of the restoration is often necessary and this demands the use of materials with a higher radiopacity. The substitution of CaO for SrO improves the material's radiopacity.

The structures of phosphate glasses and glass-ceramics are based on networks of corner sharing phosphate tetrahedra. Four types of phosphate moiety can be present, which are commonly described using  $Q^n$  nomenclature, where  $n$  represents the number of bridging oxygens (BO) of the unit. Accordingly, the  $(\text{PO}_4)^{3-}$  ( $Q^0$ ) unit has no BO, the  $(\text{PO}_{3.5})^{2-}$  ( $Q^1$ ) unit has 1 BO, the  $(\text{PO}_3)^-$  ( $Q^2$ ) unit has 2 BO, and the  $(\text{PO}_{2.5})$  ( $Q^3$ ) unit has 3 BO. These phosphorous environments can be distinguished by <sup>31</sup>P solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, due to their characteristic isotropic chemical shift ( $\delta_{\text{iso}}$ ) and chemical shift anisotropy (CSA) ranges in glass and ceramic structures [4].

In this study, a set of sodium strontium phosphate glasses and glass-ceramics, with general formula  $x\text{SrO}:(0.55-x)\text{Na}_2\text{O}:0.45\text{P}_2\text{O}_5$ , were synthesised. The crystalline phases were analysed by X-ray diffraction (XRD) and the phosphorous environment was probed by solid state <sup>31</sup>P MAS NMR spectroscopy.

## Materials and methods

Anhydrous sodium carbonate (Analar, 99.9 %), strontium carbonate (Hopkin & Williams Ltd, 98 %) and diammonium hydrogen phosphate (BDH, 97 %) were used to prepare a set of Na-Sr-phosphate glass samples of general composition  $x\text{SrO}:(0.55-x)\text{Na}_2\text{O}:0.45\text{P}_2\text{O}_5$ , with  $x = 0.00, 0.09, 0.19, 0.29, 0.39, 0.49$  and  $0.55$ , by melt quenching. The starting materials were ground as a slurry in ethanol using an agate mortar and pestle. After drying at 70° C for 3 h the mixtures were placed in platinum crucibles and heated at 300° C for 30 min to allow the release of H<sub>2</sub>O and NH<sub>3</sub>, at 650° C

for 30 min to allow the release of CO<sub>2</sub> and at temperatures between 1000-1300° C to produce the melts. After 1 h at that temperature, the melts were splat quenched in air onto a stainless steel plate.

The glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ) were measured by differential scanning calorimetry (DSC) using aluminium pans on a Perkin-Elmer DSC 7 under nitrogen atmosphere and at a heating rate of 10° C min<sup>-1</sup>.

Glass-ceramics were prepared by heating the glass samples overnight at temperatures between  $T_g$  and  $T_c$ .

The crystalline and amorphous materials were analysed by X-ray powder diffraction (XRD) on an automated Phillips PW1050/30 diffractometer, in flat plate  $\theta/2\theta$  geometry using Ni filtered Cu K $\alpha$  radiation. Data were collected from 5 to 70° 2 $\theta$ , with a step width of 0.05° and a count time of 2 s per step. Diffraction patterns were modelled by Rietveld refinement using GSAS [5].

<sup>31</sup>P MAS NMR spectra of the glasses and glass-ceramics were acquired at a frequency of 242.9 MHz on a Bruker AVANCE 600; a simple single pulse, acquire sequence was used, with a recycle delay of 60 s and a pulse width of 1  $\mu$ s which corresponds to a flip angle *ca.* 10°. 24 FIDs, each of 16384 data points were accumulated, from which, 8192 points were Fourier transformed. MAS rates were set to 12 kHz. The spectra were fitted with *dmfit* [6], to obtain  $\delta_{iso}$ , CSA and the relative concentration of each species.

## Results and discussion

<sup>31</sup>P MAS NMR spectroscopy indicated the presence of two phosphorous species in the glass structure:  $Q^1$  and  $Q^2$ . The assignment was based on the  $\delta_{iso}$  and CSA of each signal. The  $Q^1$  species, in the glass samples have  $\delta_{iso}$  from, approximately, 1.2 to -6.3 ppm, while values of CSA, ranged from 130.2 to 152.7 ppm [7].  $Q^2$  species have  $\delta_{iso}$  from, approximately, -18.5 to -22.5 ppm while values of CSA, ranged from -202.7 to 213.8 ppm [7]. The relative concentration of the two species was found to be 22 and 78 % for the  $Q^1$  and  $Q^2$  species respectively, which agrees with the values calculated from the equations developed by Van Wazer [4, 8].

The <sup>31</sup>P MAS NMR spectra of the glass-ceramic samples are shown in Fig. 1. Several different species are observed within the  $Q^1$  and  $Q^2$   $\delta_{iso}$  ranges.

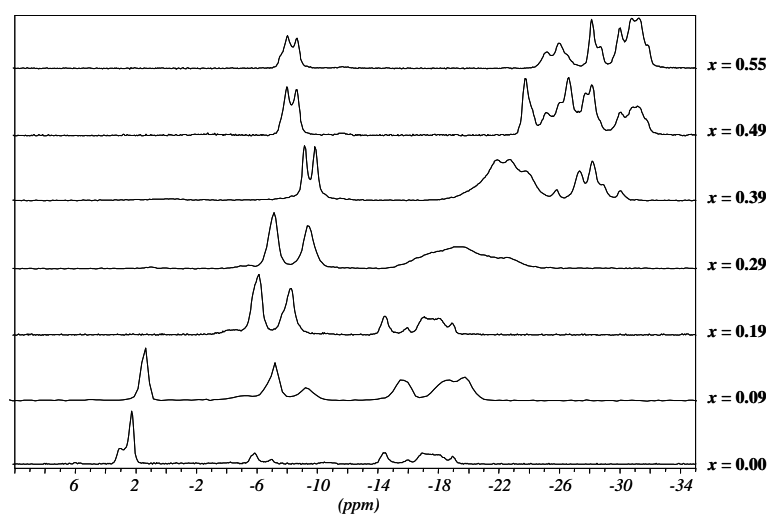


Fig. 1. <sup>31</sup>P MAS NMR spectra for glass-ceramics in the system  $x\text{SrO}:(0.55-x)\text{Na}_2\text{O}:0.45\text{P}_2\text{O}_5$ .

The changes in the spectra with change in the Sr<sup>2+</sup> concentration reflect the stabilisation of particular crystalline phases at certain compositions. At lower Sr<sup>2+</sup> concentrations ( $x = 0.00$  to 0.19) the  $Q^2$  band is mostly unchanged in isotropic chemical shift, whereas the  $Q^1$  region shows species

with lower frequency shifts dominating as  $[\text{Sr}^{2+}]$  increases. The sample with  $x = 0.29$  shows the broadest resonances and this certainly reflects the incomplete crystallisation of this sample. The spectra with the highest concentrations of  $\text{Sr}^{2+}$  ( $x = 0.39$  to  $0.55$ ) reveal a low frequency shift with  $[\text{Sr}^{2+}]$ , and small changes in the  $Q^1$  region. Turner *et al.* [9] have shown that the cation can influence the  $^{31}\text{P}$  isotropic shift in structurally related phosphate groups, according to the factor  $-Z/\sqrt{r}$ , where  $Z$  is the ionic charge and  $r$  is the ionic radius. In substituting  $\text{Na}^+$  by  $\text{Sr}^{2+}$  in the material the dominant effect is the doubling of the ionic charge, and consequently the factor is a larger number for  $\text{Sr}^{2+}$  and the negative sign results in the prediction of a shift to low frequency. Thus the changes in the spectra in Fig. 1 are consistent with the introduction of  $\text{Sr}^{2+}$  into the sodium phosphate material first producing new  $\text{Sr}^{2+}/Q^1$  crystalline phases, and at higher concentrations producing new  $\text{Sr}^{2+}$  phases.

Fig. 2 shows the XRD powder patterns of the glass-ceramics. Several stoichiometric crystalline phases have been identified and are correlated with the composition of the parent glass. Below the  $x = 0.39$  composition, sodium phosphate phases dominate the X-ray patterns, while at compositions with higher  $\text{Sr}^{2+}$  concentrations, crystalline strontium phosphates are evident.

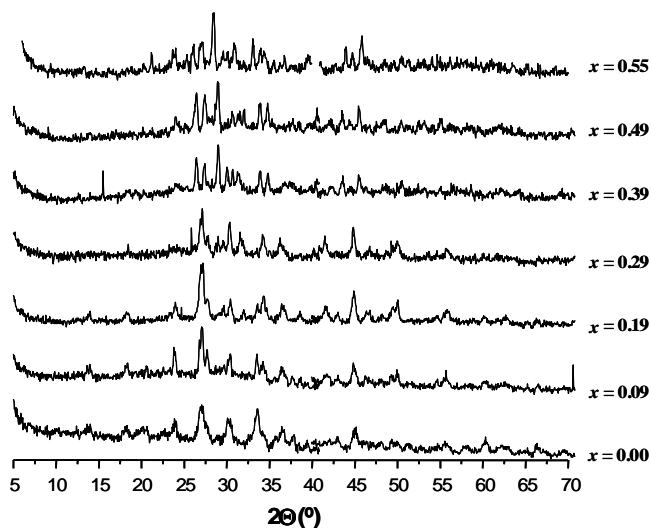


Fig.2. XRD powder patterns for glass-ceramics in the system  $x\text{SrO}:(0.55-x)\text{Na}_2\text{O}:0.45\text{P}_2\text{O}_5$ .

At the  $x = 0$  composition  $\text{Na}_3\text{P}_3\text{O}_9$  [10] and  $\text{Na}_5\text{P}_3\text{O}_{10}$  [11] have been identified as the principal crystalline phases, with some evidence of a small amount of  $\text{Na}_4\text{P}_2\text{O}_7$  [12]. As  $x$  increases,  $\text{Sr}^{2+}$  rich phases become evident and in the fully substituted system ( $x = 0.55$ )  $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$  [13] and  $\text{Sr}(\text{PO}_3)_2$  [14] have been identified. These results are consistent with the observation and variation of  $Q^1$  and  $Q^2$  species in the  $^{31}\text{P}$  NMR spectra.

Theoretically, the limiting composition at which all the  $\text{Na}^+$  ions associated with the charge balancing of the  $Q^1$  sites is with  $x \approx 0.20$ . This composition is in between samples with  $x = 0.19$  and  $x = 0.29$ , where, from the analysis of the  $^{31}\text{P}$  MAS NMR spectra the changeover from association of  $\text{Sr}^{2+}$  with  $Q^1$  species to  $Q^2$  occurs.

## Conclusion

The results indicate the preferential substitution of the  $\text{Na}^+$  cations closely associated with the  $Q^1$  phosphorous species, and only at a second stage the substitution of  $Q^2$  associated cations occur. This

conclusion is based on the  $^{31}\text{P}$  MAS NMR spectra of the glass-ceramics, where, at lower  $\text{Sr}^{2+}$  concentration the  $Q^1$  species changes its surroundings, while the  $Q^2$  species remains in a similar structural organization. This is consistent with a preferential substitution model, where the  $\text{Na}^+$  cations are closely associated with the  $Q^2$  phosphorous, while the  $\text{Sr}^{2+}$  cations are closely associated with the  $Q^1$  phosphorous tetrahedron. The non-random distribution of cations in the structure of Na-Sr-phosphate glasses reported on a previous study [7] is also observed in the glass-ceramics with similar compositions.

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