

# NMR characterization of strontium-substituted bioactive glasses and their crystallized glasses

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## Introduction

Bioactive glasses have been developed by Hench *et al* and one of them is now commercially available as Bioglass<sup>®</sup> 45S5 and widely applied in medical fields. [1] Trace amounts of inorganic ions, represented by silicate ions, have been reported to stimulate gene activation and promote bone regeneration [2].

Strontium ions have been also reported to play an important role in bone regeneration in terms of bone metabolism [3]. Since calcium and strontium ions are both divalent cations and have close ionic radius, calcium ion in Bioglass<sup>®</sup> is considered to be readily substituted with strontium ion. And the strontium-containing bioactive glasses have been proven to uptake cellular activities and are effective for bone regeneration. [4]

In the present work, CaO in the composition of Bioglass<sup>®</sup> 45S5 was substituted with SrO in series. A magic angle spinning nuclear magnetic resonance (MAS-NMR) has been employed to analyse the structures of the strontium-substituted bioactive glasses since it is useful for investigate medium range structure. Understanding the structures of glasses and crystallized glasses is important for further applications such as plasma spray coating onto implant materials. In this work, strontium-substituted bioactive glasses and their crystallized glasses were prepared and their structures were analysed using MAS-NMR.

## Materials and Methods

Glasses with nominal compositions of 46.1SiO<sub>2</sub>–2.5P<sub>2</sub>O<sub>5</sub>–(24.4–*x*)CaO–*x*SrO–26.9Na<sub>2</sub>O (mol%, *x* = 0–24.4) were prepared using a melt-quench route. (Hereafter samples are denoted by  $\gamma$ Sr using  $\gamma$ , the percentage of strontium-substitution.)

The powders of the glasses were heat treated at their onset of crystallization temperatures (T<sub>c</sub>) determined by differential scanning calorimetry (DSC) results and also

at 820 °C. The glasses and crystalline phases were examined by <sup>29</sup>Si and <sup>31</sup>P MAS-NMR and X-ray diffraction (XRD) analysis.

## Results and Discussion

The chemical shifts of the <sup>29</sup>Si MAS-NMR of the samples were summarised in Table 1.

Table 1. Chemical shifts in <sup>29</sup>Si MAS-NMR spectra of the glasses and heat treated glasses.

Glass code	<sup>29</sup> Si Chemical shift [ppm]			
	Glass	Crystallized glass		
		Heat treated at onset of T <sub>c</sub>		Heat treated at 820 °C
0Sr	-82.4	-92.4	-84.0	-91.6
25Sr	-82.6	-91.4	-84.9	-
50Sr	-79.2	-91.3	-82.7	-91.0
75Sr	-79.6	-90.9	-84.4	-
100Sr	-80.1	-90.6	-82.9	-90.5

<sup>29</sup>Si MAS-NMR spectra of the glass samples had a broad peak centered at -79 ~ -82 ppm. The peak shifted towards the low magnetic field when strontium-substitution amount increased.

Figure 1 shows that the spectra of 0Sr glass before and after heat treatments. The spectrum of glass heat treated at the onset of T<sub>c</sub> had a shoulder peak in addition to the main peak at around -92 ppm. This suggested that the sample heat treated at onset of T<sub>c</sub> includes a residual glassy phase. After heat treatment at 820 °C, the shoulder peak was disappeared and single sharp peak centered at about -92 ppm was seen. The



peak indicates  $Q^4$  or  $Q^2$  silicate in ring structure. The spectra of Sr-containing glasses were almost similar to those of 0Sr glass and crystallized ones.

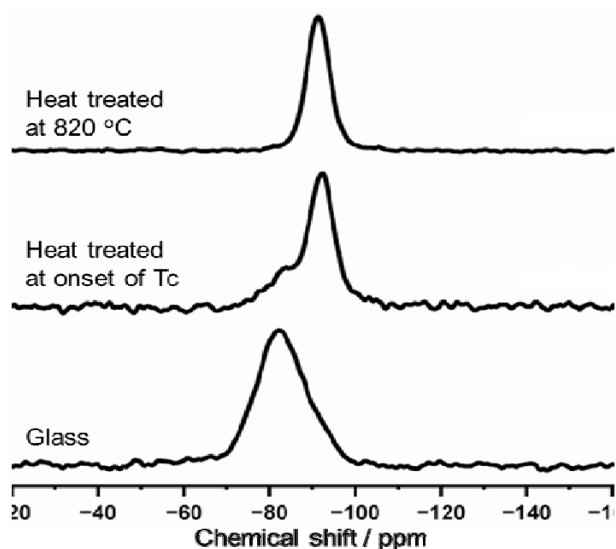


Fig.1  $^{29}\text{Si}$  MAS-NMR spectra of 0Sr glass and crystallized glasses.

$^{31}\text{P}$  MAS-NMR spectra of all glass samples had a broad and symmetric peak centered at about 8 ~ 9 ppm indicating the orthophosphate group. After heat treatment at Tc, all of the spectra included three broad peaks at 8.5, -3.0 ~ -4.5 and -20 ~ -22 ppm, which are indicative of the ortho-, pyro- and metaphosphate groups, respectively.

When strontium was included, relative intensities of pyro- and metaphosphate groups decreased and that of the orthophosphate one increased. After heat treatment at 820 °C,  $^{31}\text{P}$  MAS-NMR spectra revealed that the peak intensities of pyro- and metaphosphate phases were below their analytical levels. It seems that strontium has a tendency to inhibit phosphate-rich phases. Since all of the  $^{31}\text{P}$  MAS-NMR spectra showed the broad peaks, phosphate groups remained in glassy phase even after the heat treatment.

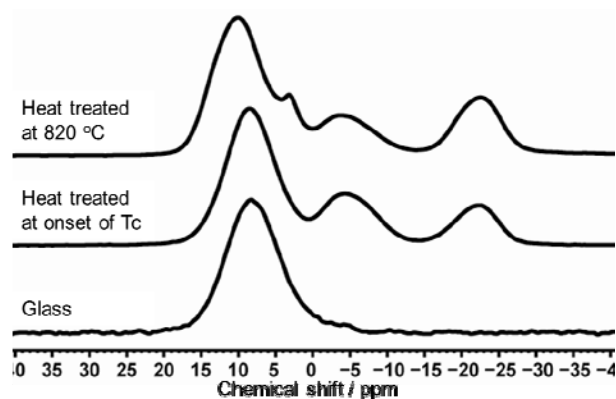


Fig.2  $^{31}\text{P}$  MAS-NMR spectra of 0Sr glass and crystallized glasses.

The XRD pattern of 0Sr glass heat treated at onset of Tc showed combeite ( $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ ) as a major crystalline phase and strontium were considered to be substituted with calcium in the combeite phase successfully, forming solid solution. The XRD pattern of 0Sr glass after heat treated at 820°C increased the sharpness of the peaks. On the other hand, in the case of the 100Sr glass, strontium silicate phase ( $\text{Sr}_3(\text{Si}_3\text{O}_9)$ ) appeared in addition to the strontium substituted combeite phase.

## Conclusions

The MAS-NMR analysis in this glass series revealed that strontium can be substituted with calcium in the glassy structure. The crystalline phases of strontium substituted glasses were identified. When glasses were heat treated, the effect of strontium-substitution became clear.

Strontium in this series has a tendency that it inhibits the formation of phosphate rich phases and promotes the inclusion of silicon to a crystalline phase as strontium silicate.

These results imply that the ion dissolution behaviour from crystallized glasses would change if these bioactive glasses would be heat treated at certain temperature.

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## References

- [1] HENCH L.L. (1991): 'Bioceramics : From concept to clinic', *J. Am. Ceram. Soc.*, **74**, pp. 1487-1510.
- [2] XYNOS I.D., EDGAR A.J., BUTTERY L.D.K., HENCH L.L. (2000): 'Ionic products of bioactive glass dissolution increase proliferation of human osteoblasts and induce insulin-like growth factor II mRNA expression and protein synthesis', *Biochem. Biophys. Res. Com.*, **276**, pp. 461-465.
- [3] MARIE P. J., AMMANN P., BOIVIN G. AND REY C. (2001): 'Mechanisms of action and therapeutic potential of strontium in bone', *Calcified Tissue Inter.*, **69**, pp. 121-129.
- [4] O'DONNELL M., CANDARLIOGLU P., MILLER C., GENTLEMAN E. AND STEVENS M. (2010): 'Materials characterisation and cytotoxic assessment of strontium-substituted bioactive glasses for bone regeneration' *J. Mater. Chem.*, **20**, pp. 8934-8941.

