

# An investigation into the structure and reactivity of calcium-zinc-silicate ionomer glasses using MAS-NMR spectroscopy

D. Boyd · M. R. Towler · R. V. Law · R. G. Hill

Received: 21 march 2005 / Accepted: 25 May 2005  
© Springer Science + Business Media, LLC 2006

**Abstract** The suitability of Glass Polyalkenoate Cements (GPCs) for orthopaedic applications is retarded by the presence in the glass phase of aluminium, a neurotoxin. Unfortunately, the aluminium ion plays an integral role in the setting process of GPCs and its absence is likely to hinder cement formation. However, the authors have previously shown that aluminium-free GPCs may be formulated based on calcium zinc silicate glasses and these novel materials exhibit significant potential as hard tissue biomaterials. However there is no data available on the structure of these glasses.  $^{29}\text{Si}$  MAS-NMR, differential thermal analysis (DTA), X-ray diffraction (XRD), and network crosslink density (CLD) calculations were used to characterize the structure of five calcium zinc silicate glasses and relate glass structure to reactivity. The results indicate that glasses capable of forming Zn-GPCs are predominantly  $\text{Q}_2/\text{Q}_3$  in structure with corresponding network crosslink densities greater than 2. The correlation of CLD and MAS-NMR results indicate the primary role of zinc in these simple glass networks is as a network modifier and not an intermediate oxide; this fact will allow for more refined glass compositions, with less reactive structures, to be formulated in the future.

## Introduction

Glass polyalkenoate cements (GPCs), used in dentistry as restorative or luting cements [1, 2], are formed by the reaction of a fluoro-aluminosilicate glass with an aqueous solution of polyacrylic acid (PAA). The acid attacks and degrades the glass structure, releasing metal cations into the aqueous phase of the setting cement. Once in the aqueous phase, these cations are cross-linked by the carboxylate groups on the PAA chains and form a cement with a microstructure consisting of reacted and unreacted glass particles embedded in a hydrated polysalt matrix [3, 4].

Although their main clinical use is in dentistry, GPCs have potential as bone cements as they eliminate many of the problems associated with conventional acrylic cements. They set without a significant exotherm, they bond directly to hydroxyapatite (HA) [5] and they have mechanical properties close to bone, which could reduce the phenomenon of stress shielding [3].

Commercial GPCs are conventionally based on aluminium glass chemistry [4]. The composition of the glass is critical to the setting of these cements and aluminium is traditionally present because it can isomorphically replace  $\text{SiO}_4$  tetrahedra within the glass structure. This causes a local charge imbalance within the structure, resulting in the acid degradability of the glass [6]. However, there are concerns over the release of aluminium from commercial GPCs as it has been identified as a potent neuro-toxin due to its ability to both disrupt cellular calcium homeostasis [7–9] and promote cellular oxidation [10]. It has also been implicated in degenerative brain disorders like Parkinson's and Alzheimer's disease [11–16]. Further to this, the use of aluminium based GPCs for reconstructive otoneurosurgery [17] and total hip replacement [18] has produced negative results; in one case patient death [19]. The replacement of aluminium

---

D. Boyd · M. R. Towler (✉)  
Materials & Surface Science Institute, University of Limerick,  
Limerick, IRELAND.  
Tel.: +353-61-213055  
Fax.: +353-61-213529  
e-mail: mark.towler@ul.ie

R. V. Law  
Department of Chemistry, Imperial College, London, UK

R. G. Hill  
Department of Materials, Minerals and Mining, Imperial College,  
London, UK

**Table 1** Glass formulations examined expressed as mole fractions.

Glass	CaO	ZnO	SiO <sub>2</sub>
A	0.35	0.11	0.54
B	0.14	0.29	0.57
C	0.28	0.32	0.40
D	0.14	0.46	0.40
E	0.05	0.53	0.42

within the glass phase of a GPC is critical if such materials are to be employed for skeletal applications.

GPCs can be formulated using glasses from the ZnO-CaO-SiO<sub>2</sub> ternary system, because zinc has the ability to work as both a network modifier and an intermediate oxide in a similar way to alumina [20, 21]. Far from acting as a neurotoxin like aluminium, the release of zinc from these cements is likely to have positive effects *in vivo* as it has the ability to increase the DNA of osteoblasts [22], resulting in increased bone mass [23]. Zinc is required for the correct functioning of the immune system and has been recognised as an antibacterial agent [24]. Therefore, Zn-GPCs have considerable potential as hard tissue replacement materials.

However, little is understood about the reactivity and setting chemistry of Zn-GPCs. It is the objective of this research to evaluate the net setting times of a selection of Zn-GPCs and relate this data to structural information taken from <sup>29</sup>Si MAS-NMR spectra of the constituent glasses in an attempt to further the understanding of the chemistry of these materials.

## Experimental

Five glass compositions were produced as illustrated in Table 1.

Glasses A to D correspond to the four eutectic points on the relevant CaO-ZnO-SiO<sub>2</sub> phase diagram [25]. Glass E was formulated to contain a minimal loading of calcium oxide.

## Glass preparation

Appropriate amounts of analytical grade silica, zinc oxide, and calcium carbonate were weighed out in a plastic tub and mixed in a ball mill (1 hour), then dried in a vacuum oven (100°C, 1 hour). Each batch was then transferred to a mullite crucible for firing (1480°C, 1 hour). The glass melts were subsequently shock quenched into demineralised water, the resulting frit being dried then ground and sieved. The glass that passed through a < 45 μm sieve was used to form the cements. Table 1 shows the chemical composition, in mole fraction, of the resultant glasses.

## Thermal characterisation

A combined differential thermal analyser-thermal gravimetric analyser (DTA-TGA) (Stanton Redcroft STA 1640, Rheometric Scientific, Epsom, England) was used to measure the glass transition temperature (T<sub>g</sub>) and the onset of crystallisation (T<sub>p1</sub>) of each glass. A heating rate of 10°C min<sup>-1</sup> was used in an air atmosphere with alumina as a reference. Analysis employed matched platinum crucibles.

## Structural characterisation

The crosslink density (CLD) of the glasses was calculated with Equation 1 using the molar compositions of the glass.

$$CLD = \frac{\text{No. BOs} - \text{No. NBOs}}{\text{Total No. Bridging species}} \quad \text{Equation 1.}$$

Where:

CLD = Cross-Link density

BO = Bridging Oxygens

NBO = Non-Bridging Oxygens

## X-ray diffraction

Powdered samples of each glass were pressed to form discs (32mm Ø x 3mm ht). Ethyl cellulose was used as a backing material. Samples were analysed using CuK<sub>α1</sub> radiation emitted from an Xpert MPD Pro 3040/60 X-ray diffraction unit (Philips, Eindhoven, Netherlands).

## MAS-NMR spectroscopy

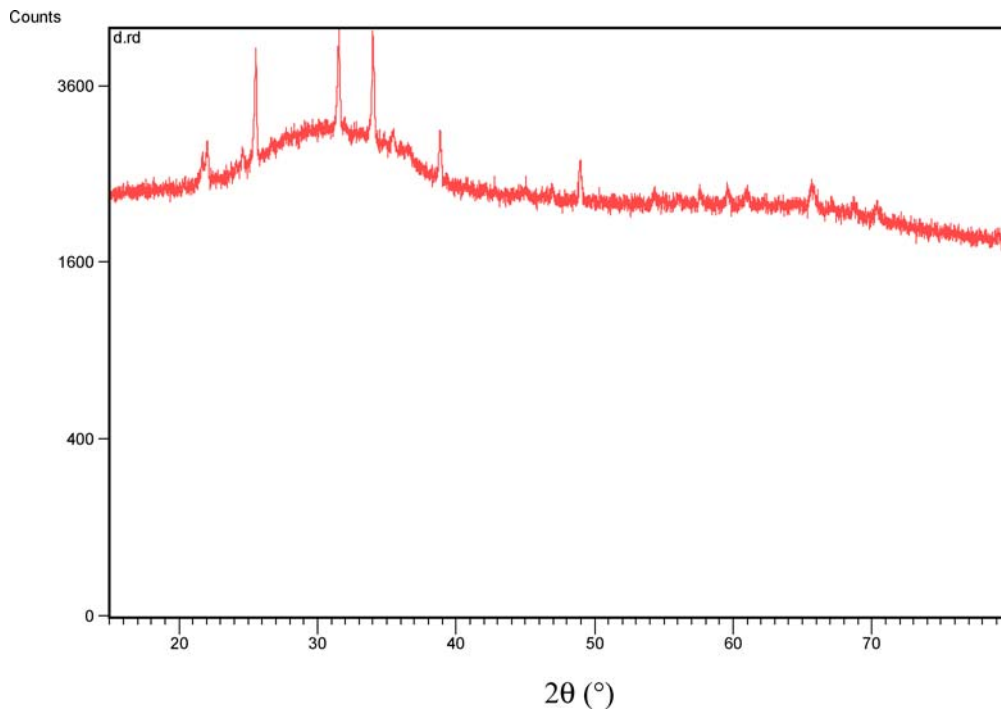
Powdered samples of each glass were examined by <sup>29</sup>Si MAS-NMR. The measurements were conducted at a resonance frequency of 39.77MHz using an FT-NMR spectrometer (DSX-200, Bruker, Germany). The spinning rate of the samples at the magic angle was 5 kHz for <sup>29</sup>Si. The recycle time was 2.0s. The reference material used to measure the chemical shift was tetramethylsilane.

## Cement preparation and evaluation

Ciba speciality polymers (Bradford, UK) supplied PAA, coded E7, in aqueous solution (25% m/w). E7, with a number average molar mass M<sub>n</sub> of 8,140 [26], was freeze-dried, ground and sieved to retrieve a < 90 μm powder. Cements were prepared by thoroughly mixing the glass powder

**Table 2** The compositions of cements examined.

Cement nomenclature	Glass employed	Glass content (g)	PAA content (g)	Water content (g)
AE7	A	1	0.195, 0.36	0.3, 0.55, 1.0
BE7	B	1	0.195, 0.36	0.3, 0.55, 1.0
CE7	C	1	0.195, 0.36	0.3, 0.55, 1.0
DE7	D	1	0.195, 0.36	0.3, 0.55, 1.0
EE7	E	1	0.195, 0.36	0.3, 0.55, 1.0

**Fig. 1** XRD pattern for glass D showing the presence of hardystonite.

(< 45  $\mu\text{m}$ ) with the PAA powder and distilled water on a glass plate. Three distinct P:L ratios (2:1, 1:0.9 and 1:1.36) were used to evaluate handling properties. Complete mixing was undertaken within 30 seconds. Glasses that were too reactive to form cements were annealed (650°C, 3 hours). The nomenclature and P:L ratios for the cements are included in table 2.

The concentrations of the PAA solutions are expressed in percent by mass (grams of solute/grams of solution).

Working and net setting times of the cements were evaluated in accordance with ISO9917E [27]. The mean setting time of three tests was recorded.

## Results and discussion

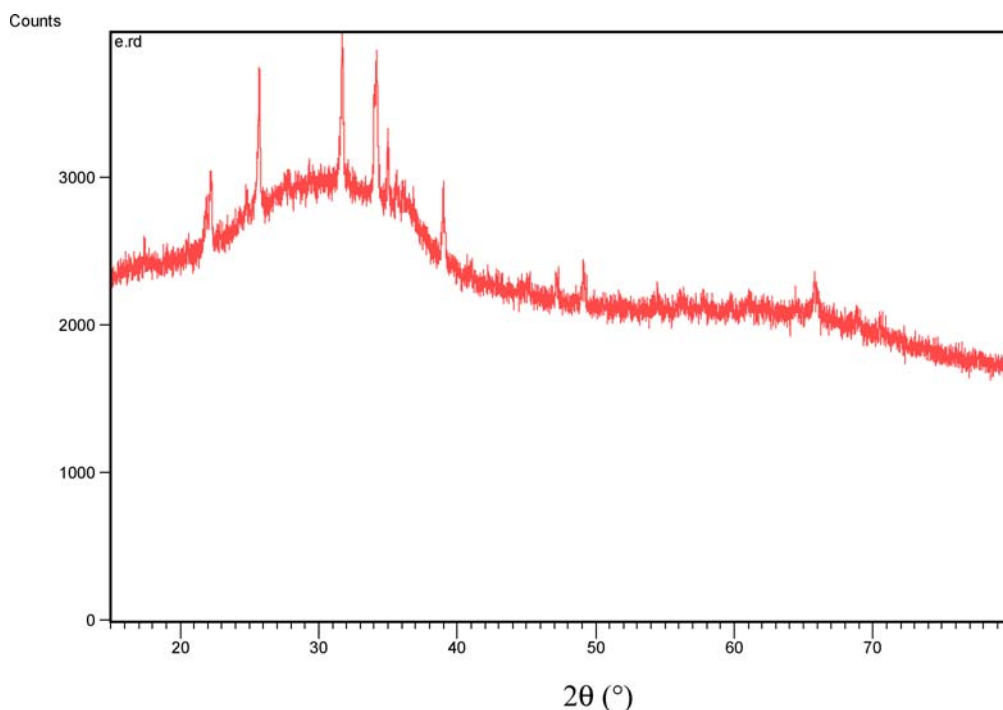
Glasses were synthesised as outlined in the methods section. Glasses A, B and C were completely amorphous in nature, whilst glasses D and E exhibited partial crystallinity

(Fig. 1 and 2). The diffraction lines for these glasses correspond with hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ ), the only ternary compound occurring in the CaO-ZnO-SiO<sub>2</sub> system [25].

## DTA and cross-link density

The  $T_{\text{gs}}$  and  $T_{\text{p1s}}$  of the glasses were evaluated by thermal analysis and are included in table 3. CLD was established as per previous literature [28] and assumes that both zinc and calcium play a network modifying role.

The low CLD of glasses D and E (Table 3) would facilitate amorphous phase separation (APS) within the glass, and the subsequent crystallization of hardystonite. Although glass C also has a low CLD, APS did not occur as expected. There is a good correlation between the CLD and  $T_{\text{g}}$  values, with the exception of glass E. The  $T_{\text{g}}$  for glass E is high relative to the other glasses. However, this is likely to be due to annealing of the glass to facilitate mixing of the cement.



**Fig. 2** XRD pattern for glass E showing the presence of hardystonite.

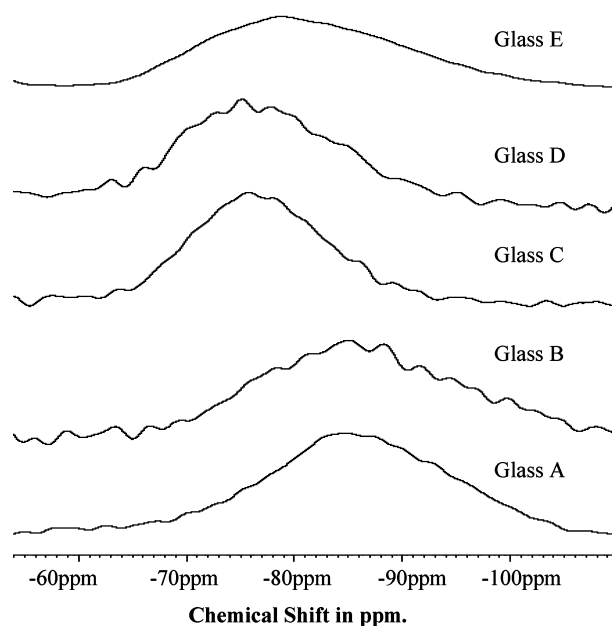
**Table 3**  $T_g$ ,  $T_{p1}$  and CLD for each glass.

Glass:	$T_g$	$T_{p1}$	CLD
A	714	885	2.29
B	680	888	2.49
C	674	806	1
D	663	771	1
E	690	779	1.23

### MAS-NMR spectroscopy

Figure 3 shows the  $^{29}\text{Si}$  MAS-NMR spectra of the glasses. The chemical shift indicates the local environment around Si atoms in the glass.

Silicon in a 4 co-ordinate state occurs between  $-60$  and  $-100$  ppm [29], with the nature of the shift depending on the number of non-bridging oxygens (NBOs) and bridging oxygens (BOs) attached to the silicon. Increasing the number of NBOs moves the peak in a positive direction due to increased shielding of the nucleus, whilst increasing the number of BOs move the peak in the negative direction due to decreased shielding [30]. For glasses A and B the chemical shift for Si occurs at  $-85$  ppm (Figs. 3 and 4). Previous literature has attributed chemical shifts at  $-86$  ppm to a  $Q_3$  structure within the glass [30, 31], but given the broadness of each peak and the calculated CLD, the predominant structures within the glass are  $Q_2/Q_3$  in nature. For glasses C and D the resonance moves toward more positive values relative to glass A and B with the chemical shift occurring at  $-75$  ppm. This indicates more shielding of the Si nucleus, corresponding to a predom-

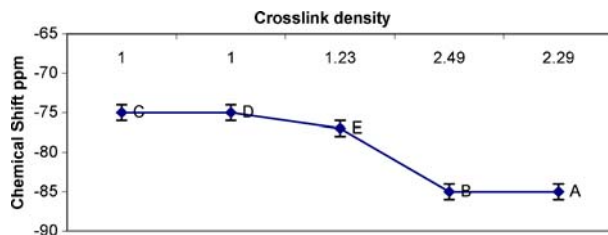


**Fig. 3**  $^{29}\text{Si}$  MAS-NMR spectra for the 5 base glasses (A-E) without strontium substitutions.

inantly  $Q_1$  glass structure, this result corresponds well with the calculated CLD of 1. As expected, these glasses exhibit the lowest  $T_g$ , indicating a highly disrupted glass network, facilitating network motion at lower temperatures. Glass E also indicates a very disrupted glass structure, with a resonance at  $-77$  ppm.  $Q_2$  structures are known to resonate at 78.9

**Table 4** Correlation of working times and setting times with glass structure (determined by MAS-NMR) and network disruption (calculated by the CLD model).

Cement	Working time (s)	Net setting time (s)	Glass structure	CLD
AE7	>7,200	>86,400	Q <sub>2</sub> /Q <sub>3</sub>	2.29
BE7	218	883	Q <sub>2</sub> /Q <sub>3</sub>	2.49
CE7	0	0	Q <sub>1</sub>	1
DE7	0	0	Q <sub>1</sub>	1
EE7	72	390	Q <sub>1</sub> /Q <sub>2</sub>	1.23

**Fig. 4** Cross-link Density as a function of chemical shift.

ppm. Given the broadness of the peak, it is fair to conclude that the structural units of this glass are Q<sub>1</sub>/Q<sub>2</sub>.

### Cement preparation and evaluation

Cement rheology was determined using a low molecular weight PAA (E7), chosen to facilitate mixing. Of the five glasses, C, D and E were found to be too reactive to form cements, however E did form a cement after annealing. Glasses A and B did not require annealing. Table 4 relates the working and setting times of cements formed from each glass with corresponding glass structure and CLD and Figure 4 plots CLD as a function of chemical shift.

The results from the working and setting times validate the structural conclusions made from the MAS-NMR and T<sub>g</sub> measurements and also correlate well with the calculated CLD values. Glass C and D could not form cements over the range of P:L ratios because the Q<sub>1</sub> glass structure will result in a very quick acid-base setting reaction that cannot form a cement. On the other hand the glass structures (Q<sub>2</sub>/Q<sub>3</sub>) in glasses A and B do facilitate a slower reaction and thus the ability to form a cement, when mixed at a P: L of 2:1, with a 40wt% solution of PAA. The setting times for cements based on glasses A and B are very different considering their similar CLD and glass structure. Cement AE7 has a setting time in excess of 2 hours, while the setting time for BE7 is just under 14 minutes. The difference is likely to be due to insufficient levels of Zn<sup>2+</sup> ions (Table 1) being released from an already zinc deficient glass composition, glass A.

Glass E only formed a cement after it was annealed. As expected from the structural analysis of glass E, the working times and setting times of cement EE7 are very short, nev-

ertheless the setting time of this basic formulation is already ISO9917 compliant as a luting cement [27].

Commercial fluoro-aluminosilicate ionomer glasses, whose rheological properties are suited to certain clinical applications, tend to have <sup>29</sup>Si resonances occurring at -90 to -99 ppm, corresponding to Q<sub>3</sub>/Q<sub>4</sub> glass structures with NC values above 3 [32]. With this in mind, and having identified the ZnO as a network modifier, it will be possible to manipulate the working times of the cement through refinement of the glass composition and structure.

### Conclusions

MAS-NMR gives essential information on the structure of ionomer glasses, with the Q<sub>n</sub> species being dependant on the composition of the glass. Comparing the calculated crosslinking density with the Q<sub>n</sub> species indicated by the MAS-NMR spectra it is fair to conclude that ZnO in these glasses acts principally as a network modifier and not as a network former. It is therefore possible to use NMR analysis of calcium zinc silicate glasses to predict the likely setting times of GPCs to be formulated from them.

### References

1. A. JOKSTAD and A. MJOR, *J. Dent.*, **24** (1996) 309.
2. J. A. WILLIAMS and R. W. BILLINGTON, *Journal of Oral Rehabilitation*, **16** (1989) 475.
3. A. D. WILSON and J. W. NICHOLSON, "Acid-base cements, their biomedical and industrial applications." (Cambridge University Press 1993.)
4. J. W. NICHOLSON, *Biomaterials*, **19** (1998) 485.
5. A. O. AKINMADE and J. W. NICHOLSON, *J. Mat. Sci. Mat. Med.*, **4** (1993) 95.
6. S. G. GRIFFIN and R. G. HILL, *Biomaterials*, **20** (1999) 1579.
7. D. JULKA and K. D. GILL, *Biochimica et Biophysica Acta.*, **1315** (1996) 47.
8. G. W. GUO and Y. X. LIANG, *Brain Res.*, **888** (2001) 221.
9. L. GANDOLFI, M. P. STELLA, P. ZAMBENEDETTI and P. ZATTA, *Biochimica et Biophysica Acta.*, **1406** (1998) 315.
10. P. ZATTA, *Coordination chemistry*, **228** (2002) 271.
11. W. F. FORBES, J. F. GENTLEMAN and C. J. MAXWELL, *Experimental Gerontology.*, **30** (1995).(1) 23.
12. J. F. GENTLEMAN and W. F. FORBES, *Experimental Gerontology*, **33** (1998) 141.
13. S. POLIZZI, E. PIRA, M. FERRARA, B. MASSIMILIANO, A. PAPALEO, R. ALBERA and S. PALMI, *NeuroToxicology*, **23** (2002) 761.
14. C. V. SWEGERT, K. R. DAVE and S. S. KATYARE, *Mechanism of aging and development*, **112** (1999) 27.
15. C. EXLEY, *J. Inorganic Biochemistry*, **76** (1999) 133.
16. P. B. MOORE, J. A. EDWARDSON, I. N. FERRIER, G. A. TAYLOR, D. LETT, S. P. TYRER, J. PHILIP DAY, S. J. KING and J. S. LILLEY, *Biol. Psychiatry*, **41** (1997) 488.
17. G. BABIGHIAN, *J. Laryngol. Otol*, **106** (1992) 954.

18. E. ENGLEBRECHT, *et al.*, *J. Bone and Joint Surgery*, **82-b** (2000).(2) 192.
19. E. REUSCHE, P. PILZ, G. OBERASCHER, B. LINDNER, R. EGENSBERGER, K. GLOECKNER, E. TRINKA and B. IGLSEDER., *Human Pathology*, **32** (2001).(10) 1136.
20. M. DARLING and R. HILL, *Biomaterials*, **15/4** (1993) 299.
21. D. BOYD and M. R. TOWLER, *J. Mat. Sci. Mat. Med.*, **Accepted** (2004).
22. M. YAMAGUCHI and T. MATSUI, *Peptides*, **17** (1996).(7) 1207.
23. J. OVESEN, B. MOLLER-MADSEN, J. S. THOMSEN, G. DANSCHER and L. MOSEKILDE., *Bone*, **29** (2001) (6) 565.
24. O. YAMAMOTO, *Int. J. Inorganic Materials*, **3** (2001) 643.
25. E. R. SEGNET, *J. Am. Ceram. Soc.*, **37** (1954).
26. A. SULLIVAN and R. G. HILL, *J. Mat. Sci.*, **35** (2000) 1125.
27. International standard 9917:1991 (E). Dental Water Based Cements. International organization for Standardization, Case Postale 56, CH-1211, Geneve, Switzerland
28. J. HENRY, M. R. TOWLER, K. T. STANTON, X. QUEROL and N. MORENO, *J. Chem. Tech & Biotech*, **79** (2004) 540.
29. A. STAMBOULIS, R. G HILL and R. V. LAW, *Journal of Non-Crystalline Solids*, **333** (2004) 101.
30. I. ELGAYER, E. ALIEV, A. R. BOCCACCINI and R. G. HILL, *J. Non Cryst. Solids* (2004).Accepted.
31. G. ENGLEHARDT and D. MICHEL, “*High-resolution solid state NMR of silicates and zeolites.*” (John Wiley and sons 1987).
32. A. STAMBOULIS, R. V. LAW and R. G. HILL, *Biomaterials*, **25** (2004) 3907.