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Preparation and characterization of bioactive sol-gel-derived $Na_2Ca_2Si_3O_9$

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In this study, pure $Na_2Ca_2Si_3O_9$ was synthesized by a sol-gel method, and $Na_2Ca_2Si_3O_9$ cuboids and disks were prepared by uniaxial pressing and calcining at 700 °C. The porosity and mechanical strength of the $Na_2Ca_2Si_3O_9$ cuboids were measured, and the results showed that the $Na_2Ca_2Si_3O_9$ cuboids were porous with an average porosity of 44%, and the 3-point bending strength of the cuboids was 6.08 MPa. The *in vitro* bioactivity of $Na_2Ca_2Si_3O_9$ was carried out by soaking $Na_2Ca_2Si_3O_9$ disks in simulated body fluid (SBF). The results showed that hydroxyapatite (HA) formed on the surface of $Na_2Ca_2Si_3O_9$ samples after soaking for 1 day, which indicated good bioactivity of $Na_2Ca_2Si_3O_9$.

1. Introduction

Bioactive glasses and glass ceramics have been widely studied during the past three decades since Hench *et al.* invented Bioglass® 45S5 [1]. When bioactive glasses and glass ceramics are implanted in human body, a bone-like HA layer forms on the surface, which has a similar composition to the inorganic part of human bone [1]. When 45S5 is heated at a temperature higher than 800 °C, $Na_2Ca_2Si_3O_9$ is identified as the only crystal phase [2–4]. Peitl *et al.* observed $Na_2Ca_2Si_3O_9$ crystals by heat-treating other Na containing glasses [5]. Although the crystallized glasses are less bioactive than the parent glasses, they are much more bioactive than commercial bioactive ceramics and glass-ceramics, which indicates that the crystal phase of $Na_2Ca_2Si_3O_9$ has a high bioactive index [5]. To our knowledge, there was no report on chemical synthesis of pure $Na_2Ca_2Si_3O_9$. In this work, pure $Na_2Ca_2Si_3O_9$ was prepared by a sol-gel method and its mechanical strength and *in vitro* bioactivity were studied.

2. Experimental

2.1. Preparation of $Na_2Ca_2Si_3O_9$

$Na_2Ca_2Si_3O_9$ was prepared using the sol-gel technique and the preparation procedure was similar to the preparation of bioactive glass 58S [6]. The sol was prepared by mixing deionized water, nitric acid (HNO_32N), tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$), calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), and sodium nitrate ($NaNO_3$) in order. The molar ratio of H_2O:TEOS was 15:1, and HNO_3 was used as catalyst for the hydrolysis of TEOS and TEP. After mixing for 1 h, the sol was sealed and aged at 60 °C for 3 days. The obtained gel was dried at 150 °C for 3 days and ball milled for 24 h, and the $Na_2Ca_2Si_3O_9$ powders were obtained by calcining at 700 °C for 2 h. The $Na_2Ca_2Si_3O_9$ powders were uniaxially compressed into disks (ϕ 6 × 2 mm) and cuboids (45 × 8 × 5.5 mm) and calcined at 700 °C for further experiments.

2.2. Characterization

The phase composition of the calcined powders was analyzed by X-ray diffraction (XRD, Model D/max 2550V, Rigaku, Tokyo, Japan) at room temperature with a monochromated Cu K_α radiation.

The porosity of the $Na_2Ca_2Si_3O_9$ cuboids was determined by the Archimedean method in carbon tetrachloride (CCl_4) according to a published procedure [7], and the 3-point bending strength measurement was conducted with a mechanical tester (Shimadza AG-5KN, Japan) at a crosshead speed of 0.5 mm/min according to the JIS R1601 standard.

2.3. Soaking in SBF

The *in vitro* bioactivity was tested by SBF soaking, and the SBF solution was prepared according to the procedure described by Kokubo [8]. The composition of SBF is listed in Table I. The experiment was carried out by soaking the disks in SBF at 37 °C for 1 h, 3 h, 6 h, 1 day, 3 days, and 7 days, respectively, and the SBF volume for each disk was 20 ml. After soaking, the disks were withdrawn from the SBF, gently rinsed with acetone and dried at room temperature. The phase composition of the surface layer after soaking was studied by thin-film XRD with grazing incidence

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TABLE I Ionic concentrations (10^{-6} mol/L) in SBF and human plasma

	Na^+	K^+	Ca^+	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5
Plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

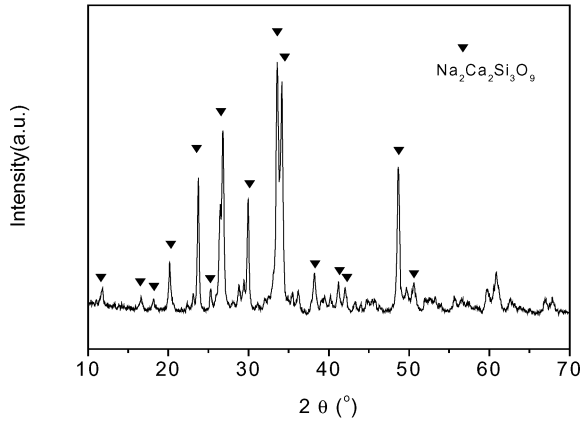

Figure 1 XRD pattern of $Na_2Ca_2Si_3O_9$ calcined at 700 °C.

θ of 2 °. The morphology of the precipitates on the samples was observed by scanning electron microscope (SEM, JSM-6700F). The soaked samples were cut into halves and embedded in bakelite powders and hot pressed into cylinders. After polished on a polishing machine (UNIPOL-801), the cross-sections of the soaked samples were observed by electron probe X-ray microanalyser (EPMA, $8705QH_2$), and the elemental distribution along the vertical direction was analyzed through EDS line scanning. The ion concentration of the SBF after soaking was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Vista AX).

3. Results and discussion

The XRD pattern of the prepared powders calcined at 700 °C is shown in Fig. 1. The crystal phase was identified as $Na_2Ca_2Si_3O_9$ and no other phase was detected. Both angular location and intensity of the peaks matched the standard PDF No. 22-1455 quite well. Like the sol-gel derived bioactive glasses, the sol-gel derived $Na_2Ca_2Si_3O_9$ cuboids were porous with a porosity of 44%, and the 3-point bending strength was 6.08 MPa. Previous studies have shown that $Na_2Ca_2Si_3O_9$ was formed in partially crystallized Na-containing bioactive glasses [2–5]. Here we demonstrated that pure $Na_2Ca_2Si_3O_9$ could be synthesized by a sol-gel method and by calcining at 700 °C.

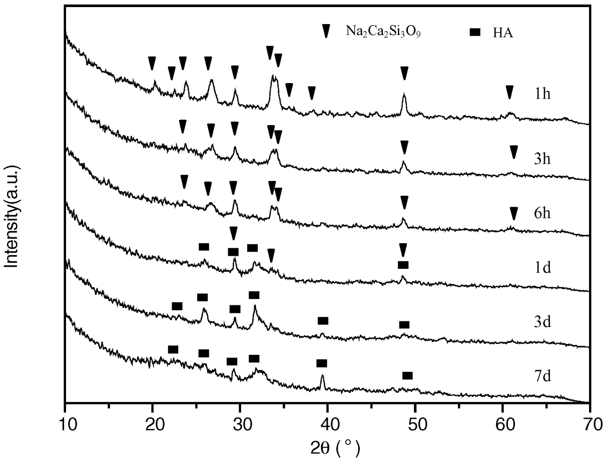

Figure 3 Thin film XRD patterns of the $Na_2Ca_2Si_3O_9$ after soaking in SBF for 1 h, 3 h, 6 h, 1 d, 3 d, and 7 d.

Fig. 2 shows the SEM micrographs of the precipitates on $Na_2Ca_2Si_3O_9$ after soaking in SBF for 3 days. The SEM micrograph (Fig. 2(a)) shows that many small spherical particles were deposited on the surface of the samples, and the high magnification micrograph (Fig. 2(b)) shows that the spherical particles were assembled from typical needle-shaped HA crystals with an average diameter of about 50 nm.

The thin-film XRD patterns are shown in Fig. 3, which revealed the phase change of the surface layer. In the first 6 h of soaking, the crystal phase in the surface layer was still $Na_2Ca_2Si_3O_9$, but the intensity of the $Na_2Ca_2Si_3O_9$ reflections decreased with soaking time. After soaking for 1 day, HA was detected. The low-intensity maxima of 2 θ at 49 °, 32 °, 29 °and 26 °C were assigned to (320), (211), (210) and (002) apatite reflections, respectively. $Na_2Ca_2Si_3O_9$ was also detected after soaking for 1 day, which indicated that

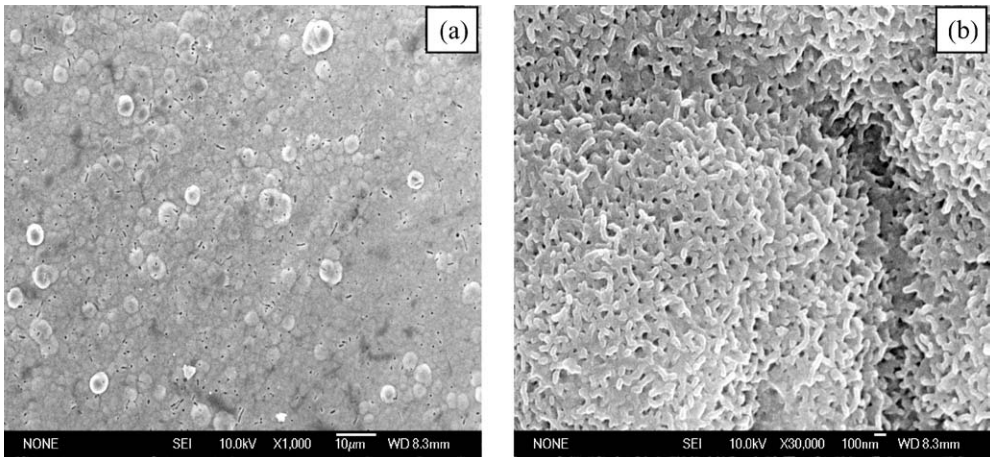

Figure 2 SEM micrographs of $Na_2Ca_2Si_3O_9$ soaked in SBF: (a) 3 days; (b) high magnification image of (a).

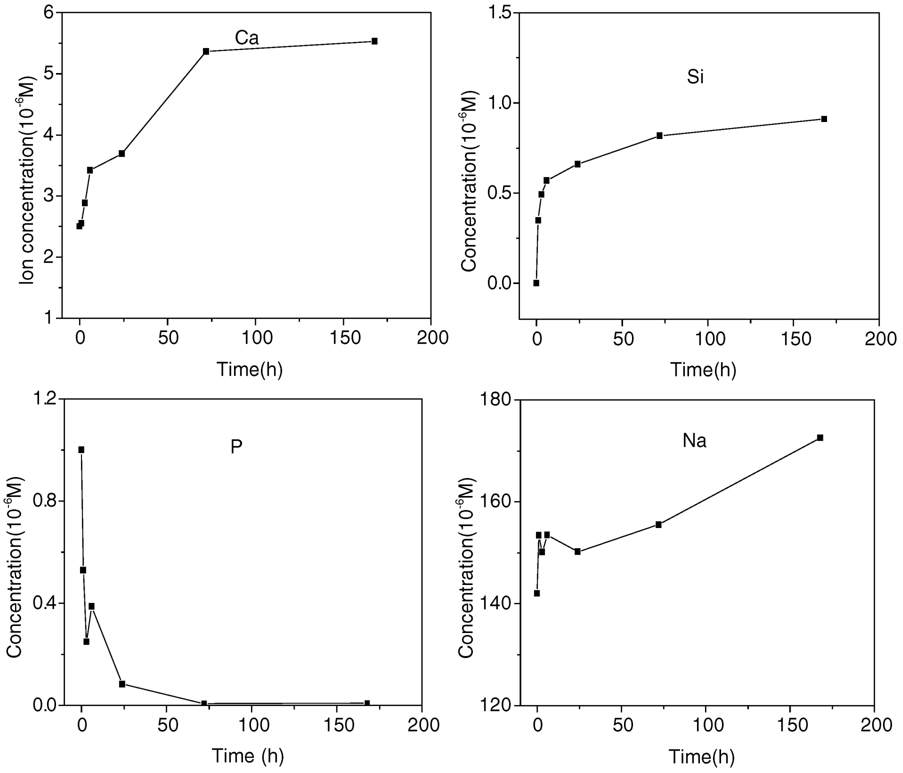

Figure 4 Variations of Ca, Si, P, and Na concentration in the SBF with soaking time.

HA did not cover the whole surface of the sample. After soaking for 3 days, the $Na_2Ca_2Si_3O_9$ diffraction maxima disappeared and the apatite diffraction maxiuma became sharper, which suggested that HA had covered the whole surface. A previous study by Filho *et al.* [2] has shown that the HA forming ability of the partially crystallized Bioglass® 45S5 containing $Na_2Ca_2Si_3O_9$ phase was lower than the amorphous Bioglass® 45S5. The HA deposition was detected on the surface of the amorphous Bioglass® 45S5 after soaking in SBF for 20 h, while on the 60% crystallized Bioglass® 45S5, HA could be detected after 40 h of soaking. Our results indicated that the pure sol-gel derived $Na_2Ca_2Si_3O_9$ possessed an equivalent HA forming ability as compared to the amorphous Bioglass® 45S5. In addition to the equivalent *in vitro* bioactivity, the pure sol-gel derived $Na_2Ca_2Si_3O_9$ may be more suitable for preparation of bulk implant materials or porous scaffolds as compared to the amorphous Bioglass® 45S5, since the pure $Na_2Ca_2Si_3O_9$ can be heat treated in a wider temperature range without phase transition.

Fig. 4 shows the variations of Ca, Si, and P ionic concentrations with soaking time in SBF solution. The calcium ionic concentration in solution increased rapidly from 2.5 ppm to 3.5 ppm during the first 6 h of soaking, and continued to increase at a lower rate and stabilized at 5.3 ppm after soaking for 3 days. The variation of Si ionic concentration was similar to that of Ca. The Si ionic concentration increased rapidly from 0 to 0.6 ppm in 6 h, and reached a constant value of 0.8 ppm after 3 days. On the contrary, the Na ionic concentration increased rapidly in the first hour, and kept increasing at a lower rate during the whole soaking period. The P ionic concentration was depleted rapidly in the first day of soaking and exhausted after soaking for 3 days. The variations in ionic concentrations in SBF indicated that the deposition of HA almost completed after 3 days of soaking, which was consistent with the results of thin-film XRD analysis.

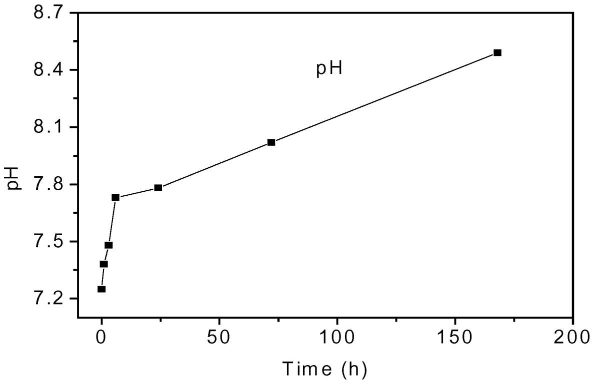

Figure 5 Variation of pH value in SBF with soaking time.

The variation of pH is shown in Fig. 5. In correspondence to the ion releasing, the pH value increased rapidly from 7.25 to 7.75 in the first 6 h, and then kept increasing at a relatively lower rate during the whole soaking period. The profile of pH increase was similar to that for Na ion release, which suggested that pH change was mainly attributed to the release of Na.

Fig. 6 shows the micrographs and elemental distribution of the polished cross-section of the $Na_2Ca_2Si_3O_9$ samples after soaking in SBF. It is clear to see that two layers with different compositions formed on the surface of the samples. The first layer was on the outer surface and enriched with Ca and P. This layer was evident after soaking for 3 h, and stabilized after soaking for 1 day (Fig. 6(b)). The second layer was rich in Si under the Ca-P-rich layer, and was 10 μm in thickness

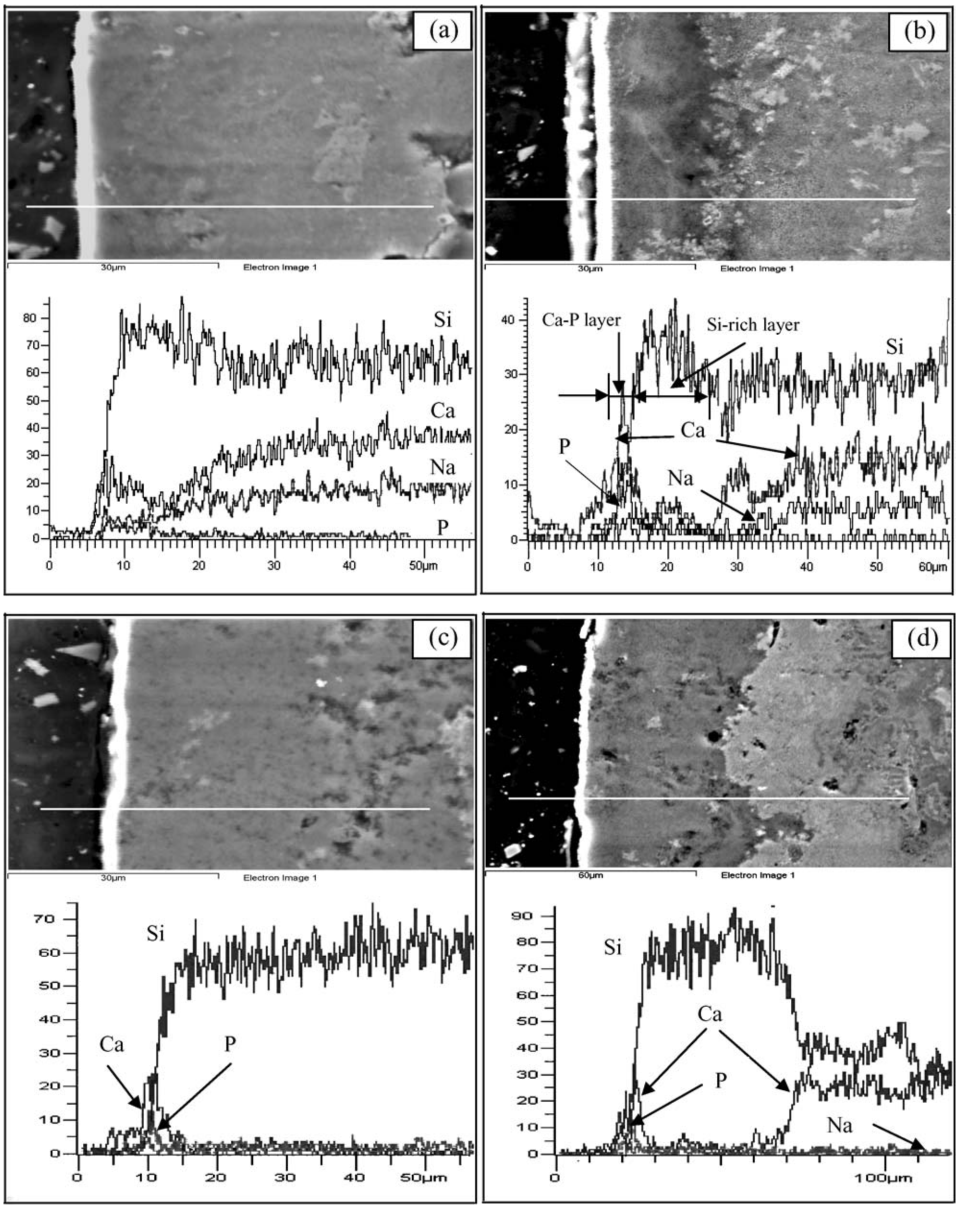

Figure 6 EPMA micrographs of the cross section and the elements distribution along the vertical direction to the surface after soaked for different periods: (a) 3 h; (b) 1 day; (c) 7 days; (d) low magnification image of (c).

(Fig. 6(b)) after soaking for 1 day. This Si-rich layer grew thicker with increased soaking time, and reached 50 μm in thickness (Fig. 6(d)) after soaking for 7 days.

Summarizing the results of XRD, ICP, SEM, EPMA, and EDS analyses, the process of HA formation can be described as follows: When the $Na_2Ca_2Si_3O_9$ sample was soaked in SBF, Na, Ca and Si in the sample rapidly exchanged with H^+ in the SBF, and formed a Si-rich layer on the surface. At the same time, Ca and P deposited on the surface of the Si-rich layer and formed an amorphous Ca-P layer, which transformed into a HA layer with prolonged soaking. This process is consistent with the process of HA formation on bioactive glasses and glass-ceramics proposed by Hench [9] and Kokubo [10].

4. Conclusions

$Na_2Ca_2Si_3O_9$ powders were synthesized by a sol-gel method, and $Na_2Ca_2Si_3O_9$ cuboids and disks were prepared by uniaxial pressing and calcining at 700 °C. The cuboids showed a porosity of 44% and a bending strength of 6.08 MPa. *In vitro* bioactivity testing showed that $Na_2Ca_2Si_3O_9$ could induce HA formation after soaking in SBF for 1 day, which indicates good bioactivity and better HA forming ability than partial crystallized Bioglass® 45S5. Our results suggest that sol-gel derived $Na_2Ca_2Si_3O_9$ might be a potential implant material.

Acknowledgments

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