Fabrication of spherical CaO–SrO–ZnO–SiO$_2$ particles by sol–gel processing

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Abstract This study was concerned with the fabrication of ceramic CaO–SrO–ZnO–SiO$_2$ spherical particles, which are novel candidates for the glass phase in glass polyalkenoate cements (GPCs). GPCs made from these glasses have potential as bone cements because, unlike conventional GPCs, they do not contain aluminum ions, which inhibit the calcification of hydroxyapatite in the body. The glass phase of GPCs require a controllable glass morphology and particle size distribution. Sol–gel processing can potentially be used to fabricate homogenous ceramic particles with controlled morphology. However, a thorough study on preparation conditions of spherical CaO–SrO–ZnO–SiO$_2$ particles by sol–gel processing has, to date, not been reported. In this study, gels were prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS) in an aqueous solution containing polyethylene glycol and nitrates of calcium, strontium and zinc. It was possible to control the morphology and size of the gels by varying the H$_2$O/TEOS molar ratio and the metal ion content in the starting compositions. An aliquot of 3–5 μm homogenous spherical particles were obtained at a H$_2$O/TEOS molar ratio of 42.6 when the starting composition molar ratios were Sr(NO$_3$):Ca(NO$_3$)$_2$: Zn(NO$_3$)$_2$:Si(OC$_2$H$_5$)$_4$ = x:0.12:(0.40 − x):0.48 (0 ≤ x ≤ 0.8). Starting composition limitations are caused by the low solubility of strontium ions in the minimal amount of water
used and the acceleration of hydrolysis as well as polycondensation at higher water content.

1 Introduction

Glass polyalkenoate cements (GPCs) are traditionally used as restorative and luting cements in dentistry [1]. GPCs are potentially useful as bone cement because they adhere to both surgical metals and the inorganic phase of bone [2]. GPCs are formed by the reaction of a glass with an aqueous solution of polyacrylic acid (PAA). The glass phase acts as a source of metal cations for the preparation of GPCs. The glass is attacked by the acid and metal cations are released from the glass structure into the aqueous matrix. These cations become trapped by the carboxyl groups of PAA chains. Cross-linking within the matrix occurs by the reaction between PAA and metal cations within the glass.

The glass phase in all commercial GPCs consist of an aluminosilicate glass [3, 4] which forms a cement by chemical reaction between aluminum ions released from the glass and carboxyl groups in the PAA. However, the release of aluminum ions has been reported to cause defective bone mineralization [5, 6] and has been implicated in the pathogenesis of degenerative brain diseases [7]. To address this issue, a glass phase free from aluminum is required. Towler et al. reported novel GPCs based on a calcium–zinc silicate glass where the zinc ion acts as both a network modifying oxide and an intermediate oxide in a similar role to the aluminum ion [8, 9]. The introduction of strontium oxide (SrO) to CaO–ZnO–SiO$_2$ glass has also been reported [10]. Strontium is a radiopacifier and has antibacterial and bone forming properties [11]. Moreover, the ionic radius of strontium is similar to that of

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calcium. A previous study reported that CaO–SrO–ZnO–SiO$_2$ glass is a precursor that offers suitable antibacterial and mechanical properties to a resultant GPC [12]. For further improvement of novel GPCs for clinical applications, more control over the glass phase composition would be required.

Sol–gel processing has several benefits for the preparation of glass and ceramic particles. Morphology can be better controlled compared to conventional melt-quenching techniques as well as lower temperature processing techniques. Recently, we reported that microspheres of a silica-based system can be obtained by sol–gel processing [13, 14] in conjunction with a water-soluble polymer such as poly (ethylene glycol). The morphology and size of the obtained particles can be controlled by the starting composition under the presence of the water-soluble polymer. In this study, we apply this process to the fabrication of CaO–SrO–ZnO–SiO$_2$ microspheres as a feasibility study to determine suitable compositions and conditions for the production of these new GPCs fillers.

2 Experimental procedure

Commercially available chemical reagents were used as reactants without further purification. Tetraethoxysilane (TEOS, Si(C$_2$H$_5$O)$_4$, Nacalai Tesque Inc., Japan) was used as the silica source. Strontium nitrate (SrNO$_3$), calcium nitrate tetrahydrate (Ca(NO$_3$)$_2 \cdot$ 4H$_2$O) and zinc nitrate hexahydrate (Zn(NO$_3$)$_2 \cdot$ 6H$_2$O) were purchased as metal sources (Nacalai Tesque Inc., Japan). 60 mass% nitric acid solution (HNO$_3$, Nacalai Tesque Inc., Japan) was used a catalyst. Poly(ethylene glycol) (PEG, Aldrich, USA) with a molecular weight of 10,000 was also employed.

All the gels were prepared by a modification of the method reported previously [13, 14]. The procedure is shown in Fig. 1. PEG and the nitrates were initially dissolved in appropriate amounts of distilled water so that various H$_2$O/TEOS molar ratios ranging from 14.2 to 56.8 were obtained at a constant PEG/TEOS molar ratio of 0.002. After the addition of a nitric acid solution, TEOS was added to the aqueous solution under vigorous stirring conditions. After stirring for 20 min, the resultant solution was transferred into a polystyrene square case and the top was tightly sealed. The case was maintained at 40°C for 1 day to allow for gelation and aging. The resultant wet gel was immersed in distilled water for 3 h to remove the PEG. The distilled water was renewed every 1 h. The wet gel was dried at 40°C for 7 days and then heated at 600°C for 2 h.

Crystalline phases of the specimens were analyzed by X-ray diffraction (RINT PC 2100, Rigaku Co., Japan). The morphology of all prepared specimens was observed using a scanning electron microscope (SEM, JSM5600, JEOL
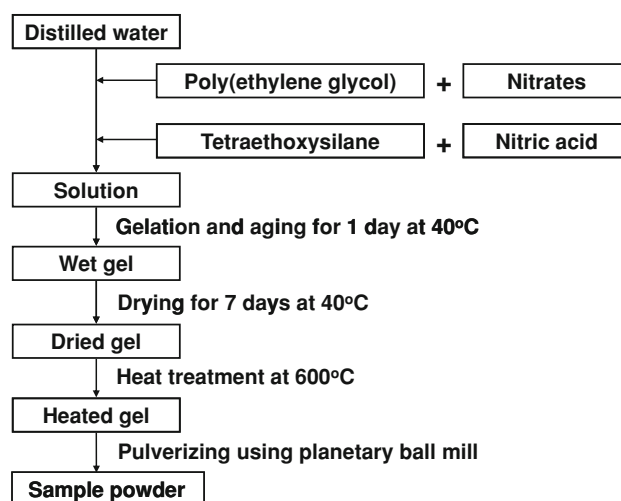

Fig. 1 Synthetic procedure for the preparation of gels in the CaO–SrO–ZnO–SiO$_2$ system

Ltd, Japan) after coating the specimens with platinum. To analyze the metal content of the gels after heating (600°C, 2 h), elementary characterization was carried out using energy-dispersive spectroscopy (EDS, EX-54140, JEOL Ltd, Japan).

3 Results

Sample compositions after solution preparation as well as after gelation and aging for various compositions are summarized in Table 1 and 2. Different amounts of water were used and the H$_2$O/TEOS molar ratio ranged from 14.2 to 56.8. The states are schematically shown in Fig. 2. The solutions free from Sr(NO$_3$)$_2$ were homogenous and they formed homogeneous white opaque bulk gels at H$_2$O/TEOS molar ratios of 14.2, 28.4 and 42.6 while the formation of a thin film phase precipitate was observed for the solution with a H$_2$O/TEOS molar ratio of 56.8 after gelation and aging. Insoluble powders were observed for the

Table 1 The starting compositions of the prepared gels

Notation	Composition (molar ratio)			
	Sr(NO$_3$)$_2$	Ca(NO$_3$)$_2 \cdot$ 4H$_2$O	Zn(NO$_3$)$_2 \cdot$ 6H$_2$O	TEOS
Sr00	0.00	0.12	0.40	0.48
Sr04	0.04	0.12	0.36	0.48
Sr08	0.08	0.12	0.32	0.48
Sr12	0.12	0.12	0.28	0.48
Sr16	0.16	0.12	0.24	0.48
Sr20	0.20	0.12	0.20	0.48

TEOS: Si(OC$_2$H$_5$)$_4$

Table 2 Appearance of the prepared samples with respect to composition

Nominal compositions of the gels*	H₂O/TEOS (molar ratio)			
	14.2	28.4	42.6	56.8
Sr00	+/+	+/+	+/+	−/+
Sr04	+/−	+/+	+/+	−/+
Sr08	+/−	+/+	+/+	−/+
Sr12	+/−	+/−	+/+	−/+
Sr16	+/−	+/−	+/+	−/+
Sr20	+/−	+/−	+/+	−/+

* Nominal compositions are given in Table 1

+/+ formation of white opaque bulk gel in homogeneous solution

+/− formation of white opaque bulk gel in solution containing insoluble powders

−/+ formation of gel film precipitated in homogeneous solution

specimens which had $Sr(NO_3)_2$ in the solutions with a H₂O/TEOS ratio of less than 14.2 and a white opaque bulk gel was obtained after gelation and aging. The composition regions increased as the H₂O/TEOS ratios increased even when $Sr(NO_3)_2$ was added to the solution but formation of the film phase precipitate was observed for all compositions of H₂O/TEOS = 56.8.

After washing and drying, the samples were heated at 600°C (2 h) and subsequently observed under SEM to determine the morphology of the prepared Sr00 gels with H₂O/TEOS molar ratios ranging from 14.2 to 56.8 (Fig. 3). Coagulation of spherical particles was observed for the
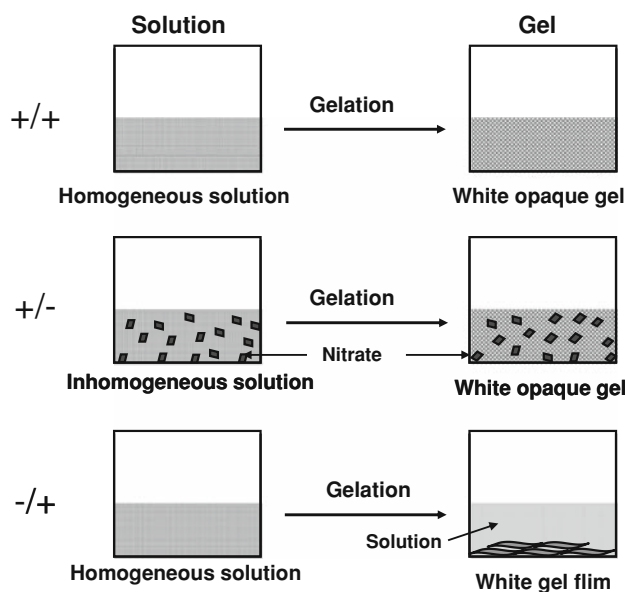

Fig. 2 Schematic drawing of the appearance of the samples prepared in this study

Sr00 samples prepared with H₂O/TEOS molar ratios of 14.2, 28.4 and 42.6 while spherical particles that were embedded in films were observed for the Sr00 sample that was prepared at a H₂O/TEOS molar ratio of 56.8. The Sr00 prepared at an H₂O/TEOS molar ratio of 56.8 had the appearance of a precipitated gel film. These results indicate that the formation of gel films is not suitable for fabrication of spherical particles for GPC glasses. Particle sizes for the
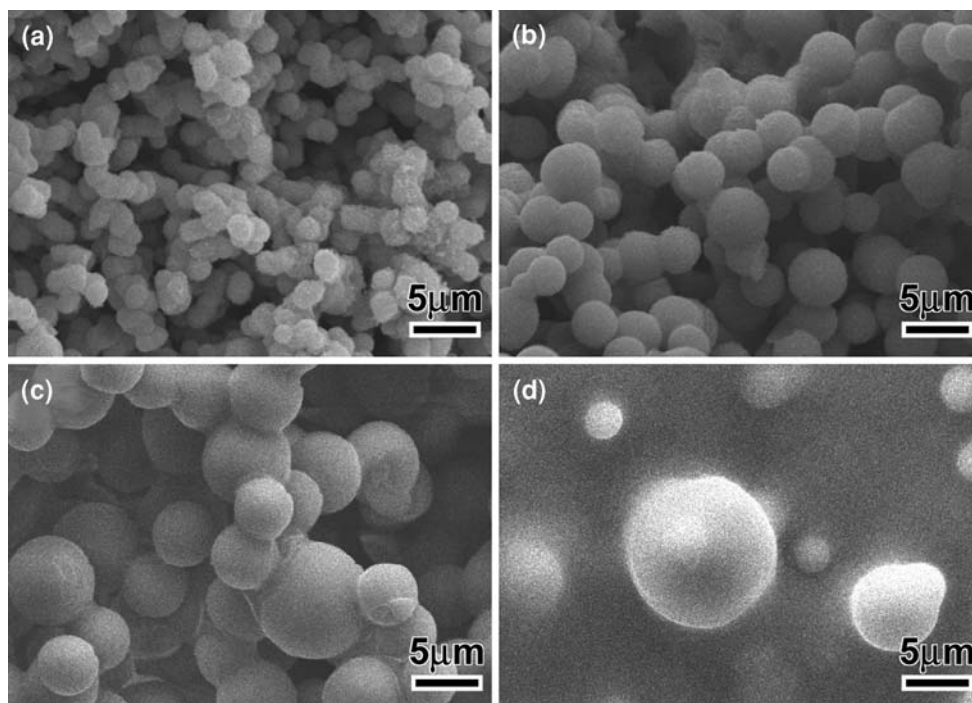

Fig. 3 SEM photographs of the Sr00 samples prepared at H₂O/TEOS molar ratios of **a** 14.2, **b** 28.4, **c** 42.6 and **d** 56.8
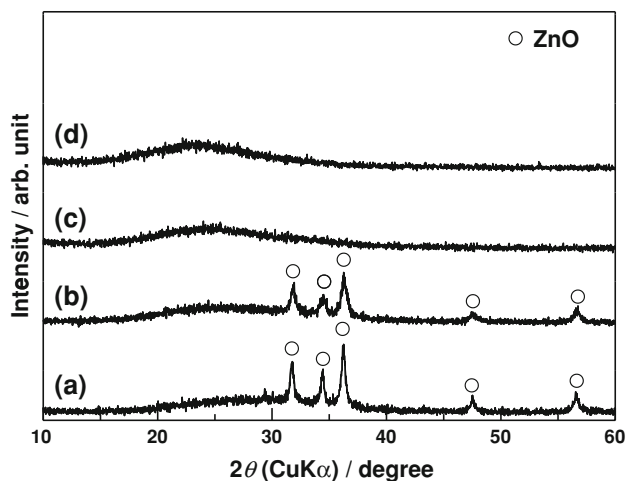
Fig. 4 Powder X-ray diffraction patterns of the prepared Sr00 samples at H_2O/TEOS molar ratios of (a) 14.2, (b) 28.4, (c) 42.6 and (d) 56.8

Fig. 6 Powder X-ray diffraction patterns of the samples prepared with various starting compositions at a H_2O/TEOS molar ratio of 42.6

Sr00 samples that were prepared at H_2O/TEOS molar ratios of 14.2, 28.4, and 42.6 increased as the water content increased. Particle sizes for the samples were 1, 3, and 5 μm for the samples with an H_2O/TEOS molar ratio of 14.2, 28.4, and 42.6, respectively. Powder X-ray diffractograms for the Sr00 samples that were prepared at different H_2O/TEOS molar ratios of 14.2, 28.4, 42.6, and 56.8 are shown in Fig. 4. Diffraction patterns for the Sr00 gels that were prepared at H_2O/TEOS molar ratios of 42.6 and 56.8 contain haloes indicating an amorphous phase, while those of the gels prepared with H_2O/TEOS molar ratios of 14.2 and 28.4 show peaks assigned to zinc oxide (JCPDS Card #36-1451). These results indicate that the insoluble
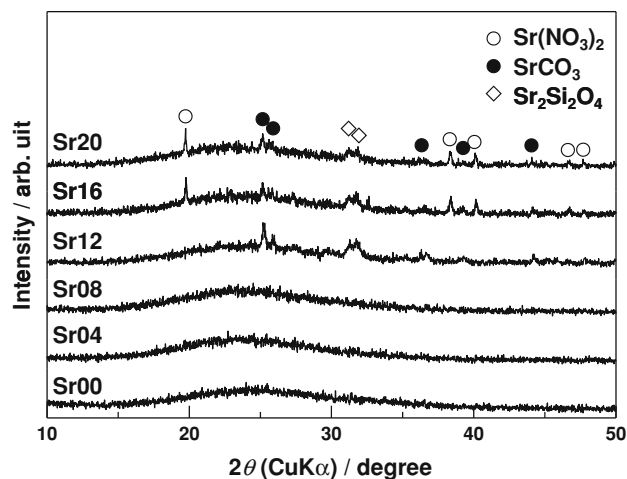
powder that was observed in solution before the gelation was a salt that contained zinc. The low amount of water used during the preparation of the solutions is not suitable for the formation of homogenous gels. The results of the preparation of Sr00 samples supports that formation of the white opaque bulk gel after homogeneous solution is most appropriate to obtain spherical particles in the process in this study.

The preparation with an H_2O/TEOS molar ratio of 42.6 allows for the widest compositional region with varying strontium content to form white opaque bulk gels after gelation and aging as shown in Table 2. Figure 5 shows SEM photographs of the samples after the preparation of
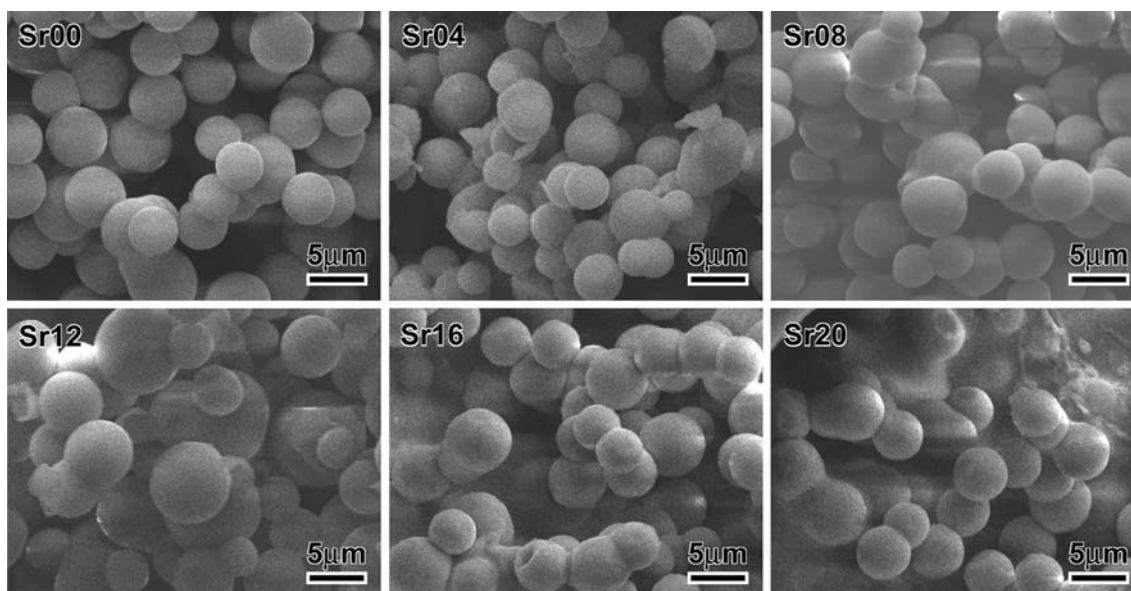

Fig. 5 SEM photographs of the samples prepared with various starting compositions at an H_2O/TEOS molar ratio of 42.6

Fig. 7 EDS results of Sr00 and Sr08 samples at a H_2O/TEOS molar ratio of 42.6
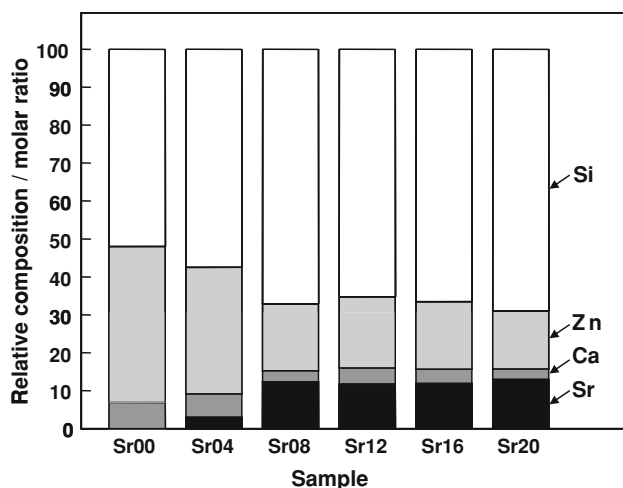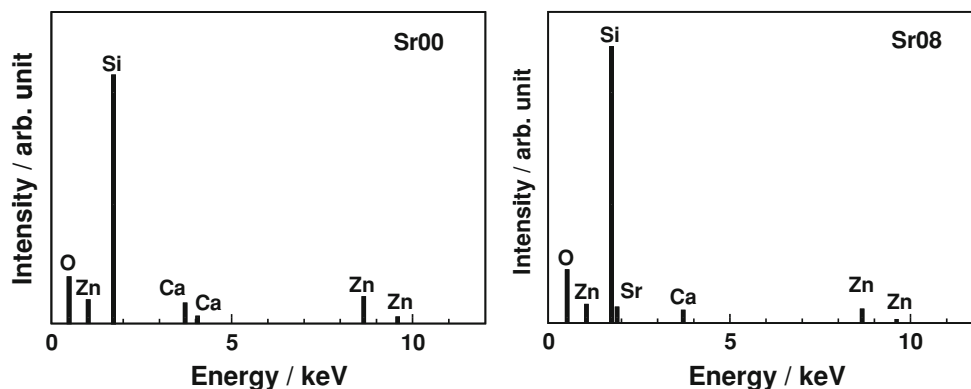

Fig. 8 The final composition of prepared samples at a H_2O/TEOS molar ratio of 42.6

the gels at an H_2O/TEOS molar ratio of 42.6 followed by heating (600°C, 2 h). All the prepared gels have a coagulation of spherical particles, approximately 5 μm in size. No significant differences among the prepared gels were evident under a constant H_2O/TEOS ratio of 42.6. The powder X-ray diffraction patterns showed that strontium compounds, $Sr(NO_3)_2$ (JCPDS Card #25-0746), $SrCO_3$ (JCPDS Card #-05-0418) and $Sr_2Si_2O_4$ (JCPDS Card #38-0271), were present (Fig. 6). This means that excess amounts of strontium formed compounds during processes such as gelation, aging and heat treatment at 600°C. The sol–gel processing used in this study allowed compositions of Sr08 or those with less strontium content at an H_2O/TEOS molar ratio of 42.6 to form a homogeneous amorphous phase with micrometer-size spherical particles.

Together with the SEM observations, the same sample sections were analyzed using EDS to determine their compositions. Figure 7 shows EDS results for Sr00 and Sr08 that were prepared at H_2O/TEOS molar ratios of 42.6 after heat treatment and these are typical examples of homogeneous amorphous particles. The Sr08 sample

contained Sr in addition to Ca, Zn, Si and O, while Sr00 contained just Ca, Zn, Si and O. All elemental analyses for the gels prepared at a H_2O/TEOS ratio of 42.6 are summarized in Fig. 8. Relative amounts of strontium increased with increasing amounts of strontium in starting compositions up to Sr08, but the relative composition of the gels prepared in the starting composition of Sr08, Sr12, Sr16, and Sr20 was almost same. The gel composition was similar for Sr08, Sr12, Sr16, and Sr20. Particles of Sr08, Sr12, Sr16, and Sr20 have similar compositions although Fig. 6 shows that crystalline phases exist and they are heterogeneous in certain parts of the gels. Gels formed from the starting compositions of Sr08, Sr12, Sr16, and Sr20 are allowed to have an upper limited content of strontium in the amorphous phase of particles.

4 Discussion

The morphology of a resultant gel from the sol–gel process, in the presence of a water-soluble polymer, depends on the starting composition [15]. In sol–gel processing, the formation of homogeneous bulk gels depends on the ratio of water to alkoxysilane (TEOS), calcium salts, zinc salts and strontium salts. Larger amounts of water facilitate the formation of a homogeneous solution but results in a precipitated gel film because of the rapid hydrolysis and polycondensation of alkoxysilane compounds. Therefore, there is an appropriate region of water content for the formation of a bulk gel. High strontium content is not allowed in this system as some crystalline phase separation occurs in the gels during this process. Therefore, a limitation for these compositions was observed during the preparation process to obtain CaO–SrO–ZnO–SiO$_2$. The sample composition that was obtained for Sr08 prepared in H_2O/TEOS was determined to be $13SrO \cdot 4CaO \cdot 17ZnO \cdot 66SiO_2$ from the EDS measurements. The value of the composition in Sr08 is less than that in the glass prepared by conventional melt-quenching techniques. The metal content in the resultant gels was generally found to be

lower than the metal content in the starting compositions. The metal ions were released to the supernatant by syneresis during aging and removed by washing with distilled water [14].

The sol–gel processing in this study allows formation of homogeneous spherical particles. The spherical particles result from a phase separation in the presence of PEG [13]. The formation of homogeneous bulk gels proceeds at a certain rate of polycondensation to induce a phase separation. After detailed reports by Nakanishi et al. [15, 16] on sol–gel processing in the presence of a water-soluble polymer, this processing was introduced to control the morphology in binary systems of $MO_{n/2}$–SiO_2 (M = Na, Mg, Ca, Al) [13, 14]. The morphology of the formed gel was controlled by phase separation which precedes polycondensation to produce siloxane networks. The fraction of silicate phase to polymer phase is a dominant parameter that determines the morphology. The rate of formation of the siloxane network was also affected by the composition of the network modifier that would be included in the gel structure. For the binary gels (CaO–SiO_2, MgO–SiO_2), the morphology of the gel changed from an interconnected-porous monolith to microspheres by increasing the metal ion content [13, 14], even when prepared at a PEG/TEOS constant molar ratio of 0.002. It is clear that the non-bridging oxygens that were formed by the addition of covalent metal ions to the siloxane network affect the skeleton of the microporous silica monolith and it is not formed. We hypothesize that SrO and ZnO act as network modifiers in the siloxane network, which is the same behavior seen when CaO and MgO are added. Strontium, calcium and zinc ions together with non-bridging oxygens lead to the formation of microspheres in silica-based binary systems under phase separation conditions [14].

Even at the same starting compositions, large amounts of water prevent the formation of bulk gel, but a gel film did precipitate. The formation of a gel film occurred at a high H_2O/TEOS content of 56.8 and this was observed for all the different starting compositions. This is attributed to rapid reaction rates since a large H_2O/TEOS ratio is known to lead to the rapid hydrolysis of TEOS [17]. Hence, the samples prepared at an H_2O/TEOS ratio of 42.6 were obtained as homogeneous glass microspheres at starting molar ratio compositions of $Sr(NO_3)$:$Ca(NO_3)_2$:$Zn(SO_3)_2$:$Si(OC_2H_5)_4$ = x:0.12:(0.40 − x):0.48 ($0 \leq x \leq 0.8$).

Although there are difficulties in controlling compositions in the resultant gels, the sol–gel process allows for the easy fabrication of spherical particles by low temperature processing. In addition, organic modification [18] is available to encourage chemical bonding to the surrounding organic matrix when the particles are used as fillers in GPCs.

5 Conclusions

CaO–SrO–ZnO–SiO_2 gels were synthesized using sol–gel processing. It was possible to control their morphologies and compositions by altering the H_2O/TEOS molar ratio in the presence of PEG. The gels prepared at an H_2O/TEOS ratio of 42.6 were obtained as homogeneous glass microspheres at starting molar ratio compositions of $Sr(NO_3)$:$Ca(NO_3)_2$:$Zn(SO_3)_2$:$Si(OC_2H_5)_4$ = x:0.12:(0.40 − x):0.48 ($0 \leq x \leq 0.8$). The size of the gels increased as the H_2O/TEOS ratio increased. The obtained SrO–CaO–ZnO–SiO_2 microspheres are expected to be useful as the glass component for the preparation of GPCs.

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