

## Preparation of an experimental glass-ionomer cements and evaluation of their properties

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**Abstract** The preparation of glass-ionomer cements based on the composition of  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--SrO--F}$  and evaluation of their properties is described. Cements were prepared via the sol–gel method and characterized by XRD, BET, SEM, and EDAX analysis. The effect of various concentrations of Sr on in vitro bioactivity of the glass specimens was investigated. In vitro bioactivity of the samples was evaluated by soaking them in simulated body fluid followed by structural characterization using SEM and atomic absorption analysis. A glass specimen with 0.5 mol of Sr exhibited appropriate bioactivity.

**Keywords** Glass-ionomer cement · Strontium · Bioactivity · Compressive strength (CS) · Simulated body fluid · EDAX analysis

### Introduction

After the invention of glass-ionomer cements (GICs) by Wilson and Kent in the early 1970s [1–3], the preparations of these materials have been of considerable interest because of their use as a dental restorative material [4–6], and due to their unique properties such as coherency to tooth structure and base metals [7, 8], biological compatibility, and low cyto-toxicity [7, 8]. GICs have low coefficients of thermal expansion similar to that of tooth structures, which causes good thermal compatibility with tooth enamel and dentin [9]. When fluoride is released to GICs, they show anti-cariogenic properties [10]. In addition, they minimize micro-leakage at the tooth–enamel interface due to low shrinkage [11, 12]. Because of their wide range of applications especially in dentistry, significant improvements have been

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made since the invention of GICs, and further improvements are required in order to increase their physical properties.

Historically, two common procedures have been developed for the preparation of GICs [13–26]. The main composition of the glass first studied by Wilson and Kent [1–3] was calcium-fluoro-alumino-silicate which was prepared via a conventional fusion method at high temperatures (ranging from 1,100 to 1,550 °C). This method has some problems such as uncontrolled fluorine losses during melting which causes the prepared glass to have a variable composition [1–3]. This problem can be surmounted by the use of chemical methods such as the sol–gel process which is more advantageous due to composition control and chemical homogeneity.

In recent times, new formulations of glass have been developed for use as cement formers, also using the sol–gel technique. In this context, the objective of this paper is the preparation and evaluation of the properties of GICs containing strontium.

## Experimental

### Reagents and instrumentation

All reagents were purchased from Merck and Aldrich and used without further purification. The powder X-ray diffraction patterns were measured with a D8 Advance diffractometer (Bruker) using Cu-K $\alpha$  irradiation. SEM photographs coupled with EDAX analysis were taken by a Philips XL30 model to examine the shape of the precursor powders and GICs. XRF analysis was done by a Bruker X-ray fluorescence spectrometer (S4 PIONEER). Atomic absorption data were collected using a Varian atomic absorption spectrometer (AA-220).

### Preparation of precursor powder of GICs

The precursor powder was prepared using the sol–gel method. Typically, tetraethyl orthosilicate (TEOS) was first hydrolyzed in ethanol under continuous stirring at room temperature for 1 h. The previously dissolved aluminum and calcium salts in water were then added drop-wise to the hydrolyzed TEOS solution. In sequence, strontium citrate solution and fluorosilicic acid were added to the solution. The fully mixed solution was then heated with continuous stirring to 80 °C, until gelation occurred. In order to obtain the powder sample, the gel was dried at 80 °C, pulverized, and then heated at 600 °C for 2 h using an electrical furnace. The prepared powder was then ready for future characterization.

### Cement preparation

The GICs containing strontium were synthesized following the procedure described elsewhere [27], with a slight modification. Typically, the experimental powder after the undergoing the heating process at 600 °C was passed through a sieve and was then used to produce the cements. The experimental GICs were prepared at room

temperature by mixing the powder with aqueous solutions of 50 % (m/m) of poly(acrylic acid) and aqueous solution (10 % m/m) of tartaric acid. The commercial restorative specimens were made using a powder:liquid (P:L) ratio of 2:1 (m/m) according to the manufacturer's instructions.

## Results and discussion

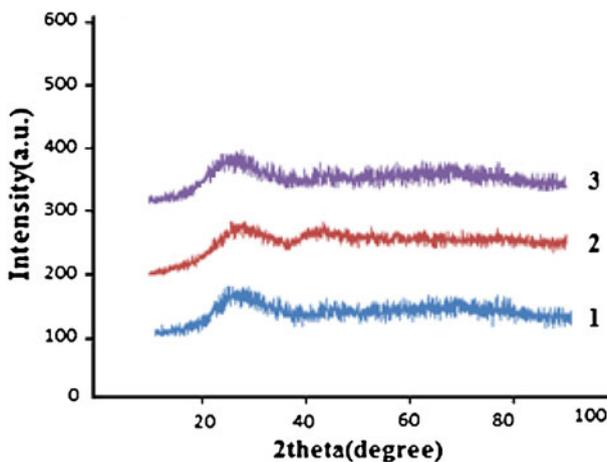
### Preparation and characterization of precursor powders

The precursor powder of the GICs was prepared using the sol–gel method containing 0.5–1.5 mol of SrO.

The powders prepared were analyzed by X-ray powder diffraction (XRD) to identify the crystal phases. The XRD pattern of the as-prepared powders (for one of them; the others are the same) is illustrated in Fig. 1. As can be seen, all the systems are amorphous as can be expected for glass. This behavior indicates that the addition of strontium does not have a strong influence on the vitreous characteristic of GICs. Regardless of the amount of SrO present in our systems, no crystalline phase was observed after the calcination process.

The chemical composition of as synthesized precursor powders was determined using XRF analysis as shown in Table 1. The XRF analysis confirmed the presence of strontium, and the amount of SrO in the precursor powder samples varied from 5.71 to 14.42 %. The losses of compound during the ignition processes were 5.78, 7.59, and 7.37 for precursor powders 1–3, respectively.

A scanning electron micrograph coupled with EDAX analysis (SEM–EDAX) for the precursor powder sample 3 has been provided. The SEM image of sample 3 is illustrated in Fig. 2. From Fig. 2, it is revealed that the powder is in the nano-sized range and irregular in shape.

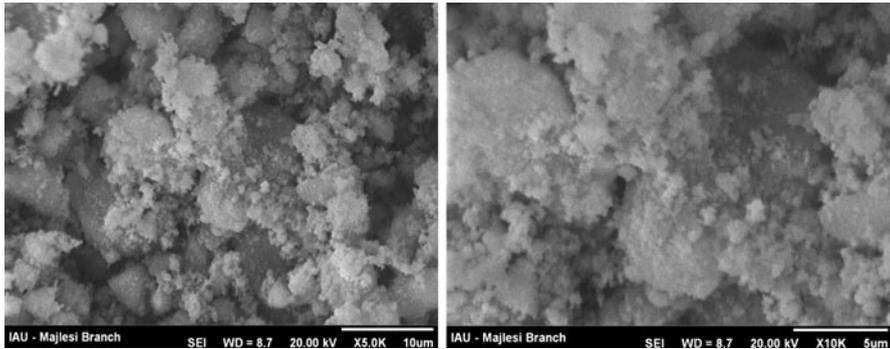
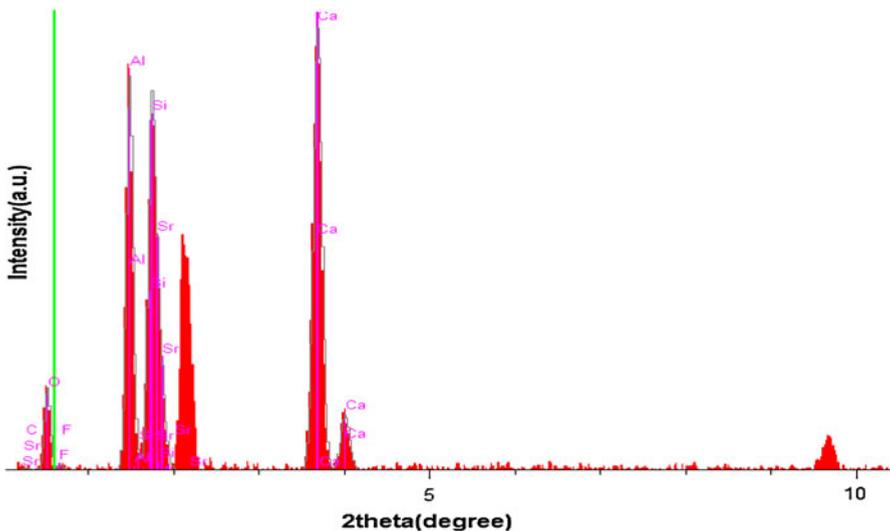


**Fig. 1** XRD patterns of the as-synthesized precursor powders 1–3

**Table 1** XRF analysis of the as-prepared precursor powders

Precursor powder samples	Chemical composition						Total
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SrO	F	LOI <sup>a</sup>	
1	24.71	28.75	31.25	5.71	3.80	5.78	100
2	26.32	29.83	22.13	10.10	4.03	7.59	100
3	25.09	28.04	20.98	14.42	4.10	7.37	100

<sup>a</sup> Loss on ignition

**Fig. 2** SEM micrographs of precursor powder 3**Fig. 3** EDAX analysis of precursor powder 3

The EDAX image of the sample 3 is shown in Fig. 3. It was performed to identify the elemental composition of the sample 3, and their results are summarized in Table 2 which is relatively identical with the result of XRF analysis.

**Table 2** Elemental analysis for the precursor powder 3 calculated via EDAX analysis

Element	Intensity	Density (wt %)
O	65.07	27.241
F	4.14	1.292
Al	357.63	15.234
Si	314.52	14.516
Ca	515.70	23.333
Sr	125.12	16.627
Impurity	–	1.757
Total		100

**Table 3** Specific surface area of the precursor powders 1–3 ( $\text{m}^2/\text{g}$ )

Precursor powder	Surface area
1	47.28
2	46.53
3	46.20

The determination of the surface area of the investigated samples was carried out in situ by the BET adsorption isotherm method using nitrogen as the adsorbate. The BET surface area was determined to be 47.28, 46.53, and 46.20 ( $\text{m}^2/\text{g}$ ) for the precursor powders 1–3, respectively (Table 3).

### Preparation of GICs

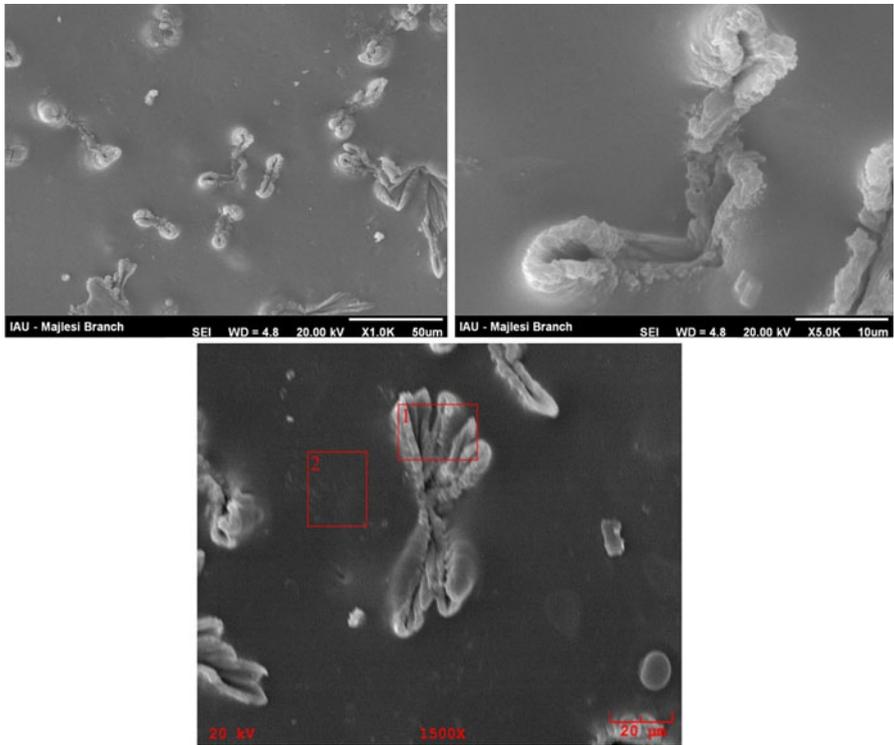
The GICs were prepared following the procedure described elsewhere [27], with a slight modification, at room temperature. The precursor powders were mixed with aqueous solutions of poly(acrylic acid) (50 % m/m) and aqueous solution of tartaric acid (10 % m/m). The powder:liquid (P:L) ratio was chosen as 2:1 (m/m).

A SEM image coupled with EDAX analysis was applied to identify the chemical composition of GICs.

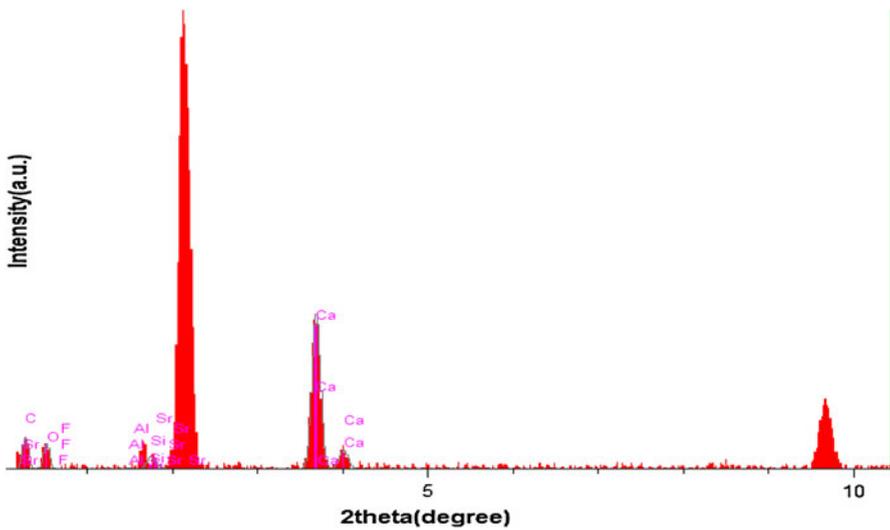
The morphology of GIC 3 prepared from the mixing of precursor powder and aqueous solution of poly(acrylic acid) and tartaric acid was measured and presented as shown by SEM images in Fig. 4.

The EDAX analysis result which is illustrated in Fig. 5 and Table 4 confirmed the presence of Sr and shows the percentage of elementals of GIC 3. The existence of carbon is related to the carboxylic acids including poly(acrylic acid) and tartaric acid.

The mechanical strength results of GICs 1–3 (CS) is shown in Fig. 6. Figure 6 shows the effect of Sr on CS values of the cements. By comparing the cements containing Sr with those without Sr, it is clear that cements containing Sr showed statistically higher CS. Among the GICs containing Sr, sample 1 (0.5 mmol Sr) has higher CS values. Increasing the amount of Sr on the GICs decreased the CS values of the cements. This is due to the lack of appropriate reaction between the ceramic component and polymeric liquid and complete hardening of them. So there is



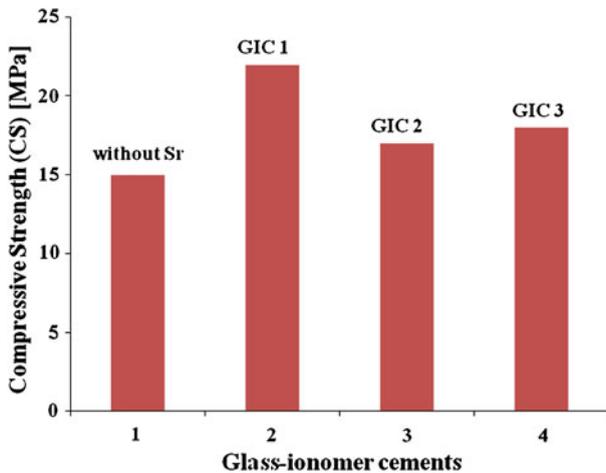
**Fig. 4** SEM micrographs of GIC 3



**Fig. 5** EDAX analysis of GIC 3

**Table 4** Elemental analysis for the GIC 3 calculated via EDAX analysis

Element	Intensity	Density (wt %)
C	25.61	21.745
O	19.70	44.227
F	1.01	0.026
Al	1.12	0.244
Si	10.68	1.899
Ca	173.89	30.362
Sr	3.07	1.497
Total		100

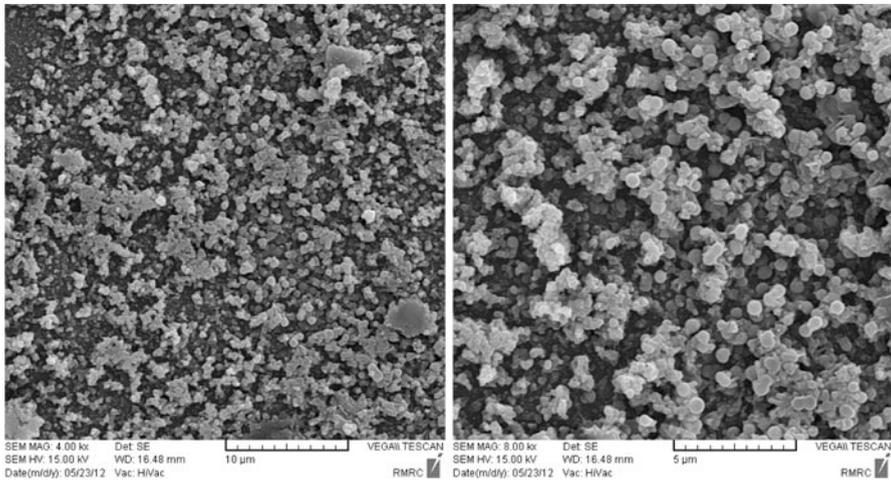
**Fig. 6** The CS values of GICs with and without Sr

usually an increase in compressive strength, but, on the other hand, due to the constraint which occurred in the hardening reaction of the glass-ionomer cement, creates a loss in compressive strength.

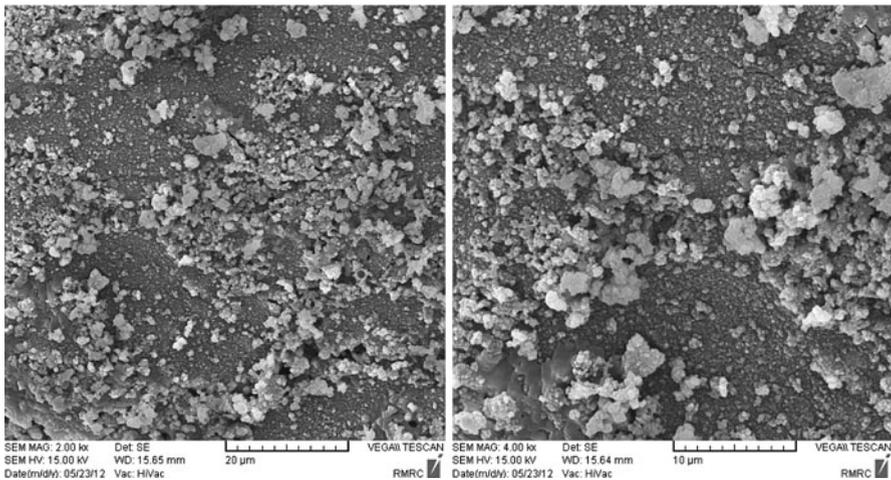
#### Bioactivity behavior of glass ionomer cements in simulated body solution (SBF)

For evaluation of the bioactivity behavior of GICs, samples were immersed in tris-buffered simulated body fluid (SBF). The SBF solution had a chemical composition and concentration similar to the inorganic part of human plasma. The samples were kept in this solution at 37 °C for 28 days. At the end of 28 days, the whole volume of the SBF was extracted for measurement and the study of its Ca and Sr content using SEM images and atomic absorption analysis. The changes in concentration of Ca of the extracted SBF solution were measured by the atomic absorption technique.

The surface morphologies of the specimens were observed by scanning electron microscope (SEM). Because of the poor electrical conductivity of the samples, their

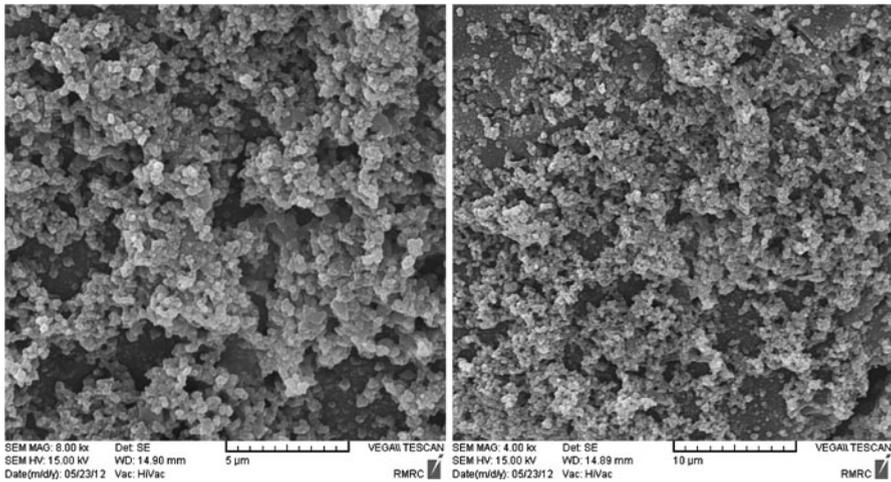


**Fig. 7** SEM micrographs of GIC 1 after being kept in SBF solution at 37 °C for 28 days



**Fig. 8** SEM micrographs of GIC 2 after being kept in SBF solution at 37 °C for 28 days

surfaces were coated with a thin layer of gold before the test. The images show that apatite formation on the surface of the cement has occurred. The SEM images of the GICs 1–3 are shown in Figs. 7, 8, 9, which show that tiny agglomerated particles thought to be hydroxyl apatite occurred on the surface of the GICs soaked for 28 days. The structure of this layer consists of loosely packed agglomerates presenting a rough surface. The results showed that the presence of Sr in the glass composition retards formation of the apatite layer onto the glass surfaces. Morphologies of the apatite layers were also different as the abundance of the crystals decreased with increasing Sr concentration.



**Fig. 9** SEM micrographs of GIC 3 after being kept in SBF solution at 37 °C for 28 days

**Table 5** Atomic absorption analysis of GIC 3 after being kept in SBF solution at 37 °C for 28 days

Material	Ca ion concentration
Reference	35.1 ppm
GIC 1	38 ppm
GIC 2	52.8 ppm
GIC 3	37.3 ppm

The results of atomic absorption analysis are summarized in Table 5, which shows that the calcium ion concentration in simulated body solution (reference sample) is 35.1 ppm, while the concentration of calcium ions in the solution after 28 days of immersion of GICs 1–3 in SBF increased to 38, 52.8, and 37.3 ppm respectively. It can be seen from Table 5 that all the GICs cause an increase in the calcium concentration of the SBF. Among the GICs, GIC 2 showed the largest increase in calcium concentration. The increased concentration of calcium ions in the SBF indicates that the calcium component was released from the cement specimen. The Ca ion is a precursor for the formation of hydroxylapatite. The results indicate that the addition of various amounts of strontium in ceramic glass-ionomer cement improved the biological properties of the samples.

## Conclusion

The preparation and evaluation of experimental GICs containing strontium were investigated. Experimental cements were prepared by mixing a precursor glass powder and an aqueous solution of poly(acrylic acid) (50 % m/m) and aqueous solution of tartaric acid (10 % m/m) with the powder:liquid (P:L) ratio of 2:1 (m/m). The chemical composition of GICs was identified using SEM coupled with EDAX

analysis. When the strontium content was increased from 0.5 to 1.5 mol, the CS values of the synthesized GICs decreased. In comparisons, the CS of the experimental cement containing Sr is higher than that without Sr. This indicates that the addition of strontium content to the structure of GICs could enhance the mechanical properties of this type of material. For evaluation of the bioactivity behavior of GICs, samples were immersed in tris-buffered simulated body fluid (SBF). The results showed the effect of the presence of Sr on the formation of an apatite layer onto the glass surfaces. Based on this study, the prepared bioactive glass-ionomer cements might be useful for regenerating tooth structures.

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