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# Effect of strontium-to-calcium ratio on the structure, crystallization behavior and functional properties of diopside-based glasses

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ABSTRACT

The role of Sr/Ca ratio, which was varied from 3/6 to 9/0, on the structure, crystallization behavior and properties of diopside-based glass and glass-ceramic sealants targeted to solid oxide fuel cell (SOFC) applications was evaluated. The structural changes undergone by glass-powder compacts during isothermal heat treatment at 850 °C for 1–1000 h were investigated using XRD (X-ray diffraction) analysis, including quantitative Rietveld refinement, and MAS-NMR (magic angle spinning nuclear magnetic resonance) techniques. The tendency towards crystallization was retarded with increasing Sr/Ca ratio. Diopside-based phases, strontium akermanite and magnesium silicate were developed under various heat-treatment conditions. MAS-NMR analysis of glasses heat treated for 1000 h revealed that with increasing Sr/Ca ratio, $Q^1$ and $Q^4$ structural units were formed at the expenses of $Q^2$ units. The good thermal stability and chemical compatibility of the new glass-ceramic compositions coupled with their mechanical reliability and high electrical resistivity make them attractive for further experimentation as sealants for SOFCs.



## 1. Introduction

During the last decades, continuous and significant world-wide efforts have been made on the investigation of reliable sealants for solid oxide fuel cells (SOFCs) [1–4]. Glasses/glass-ceramics have emerged as promising materials for this application because of their ability to form hermetic seals at high temperatures [1–4]. Among the various types of glass/glass-ceramic sealants, alkaline-earth aluminosilicate glasses have shown their superiority [5]. However, the key issue with the glass/glass-ceramic sealants is their thermal stability towards devitrification and chemical interactions with ceramic/metallic plates during the long-run heat treatment at SOFC operating temperature. Most of the alkaline-earth alumino-silicate glasses are prone to devitrify at higher temperatures

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(600–900 °C) during long operation times [5–8]. This results in continuous variations in the properties of glass/glass-ceramics that affect the performance of SOFC stacks. Although controlled devitrification is a prerequisite for a suitable sealing-glass composition, the formation of some undesirable crystalline phases in the glass seal can severely affect the performance of SOFC stacks. For example, barium-rich aluminosilicate based glass seals [9,10] are known to exhibit appropriate thermal behavior when SOFCs start operating. However, these glasses tend to devitrify at 800–850 °C resulting in the appearance of hexacelsian ($BaAl_2Si_2O_8$) crystalline phase in the glass-ceramic, which then gradually transforms during SOFC operation into its monoclinic polymorph with a low coefficient of thermal expansion (CTE) [11]. Similarly, severe chemical interactions have been observed at the interface between BaO-containing or alkali-containing glass seals when joined with the metallic interconnects of SOFCs [12,13].

Overcoming the above-mentioned limitations requires searching for alternative Ba-free glasses. In this regard, Hao et al. [14] have reported the enhanced wetting ability of SrO-containing glasses in comparison to BaO-containing glass compositions. Mahapatra and Lu [15] proposed the development of SrO-containing lanthanum aluminosilicate glass (SABS-0) possessing all the desired thermophysical properties. Stable electrical resistivity in both air and reduced atmosphere has been reported for SrO-containing alkaline-earth yttrium silicate glasses [16]. Based on thermodynamic considerations, other authors [17] found that $Sr^{2+}$ ions are more stable in crystalline form than they are in the glass matrix within the operational temperature range of SOFCs [17]. According to earlier reports [18,19], the thermal properties of glass sealants depend exclusively on the network structure of the glass. However, the role of $Sr^{2+}$ in glass chemistry is still far from being well understood and continues to be a matter of debate. Since $Sr^{2+}$ ions in glass-ceramics and their distribution among the amorphous/crystalline phases affect the thermal behavior of the material, further research concerning the role of strontium in glasses is necessary.

Recently, a series of glasses in which partial substitution of Ca by Sr up to 40 mol% in a diopside-$BaSi_2O_5$ boron-containing glass system were proposed and their suitability for sealing applications was investigated [20,21]. The resultant glass-ceramic materials were revealed to be suitable candidates for rigid glass-ceramic-based sealants, as sufficient electrical resistivity coupled with an absence of oxygen leakage could be measured through dense glass-ceramics. Moreover, good thermal stability of Sr-diopside and a maximum CTE value ($\sim 10.7 \times 10^{-6}$ $K^{-1}$) were obtained when 40 mol% $Sr^{2+}$ ion substituted for $Ca^{2+}$ ions. These further interesting features stimulated us to investigate the effects of higher levels of Sr-substitutions. The present work focuses on boron free compositions with the extension of Sr for Ca substitution up to 100% in $Ca_{0.9}MgAl_{0.1}La_{0.1}Si_{1.9}O_6$ component of the parent diopside-$BaSi_2O_5$ glass [20,21], and evaluation of the effects of the Sr/Ca ratio on the structure, crystallization behavior and functional properties.

## 2. Experimental procedure

The chemical compositions of the experimental glasses with Sr/Ca ratios of 3/6, 5/4, 7/2 and 9/0 are presented in Table 1. The detailed glass synthesis procedure was mentioned elsewhere [20]. Glasses in frit form were obtained by quenching of glass melts in cold water followed by drying and milling in a high-speed agate mill, resulting in fine glass powders with mean particle sizes of ~10–20 μm (determined by light scattering technique; Coulter LS 230, Beckman Coulter, Fullerton, CA; Fraunhofer optical model). The onset of crystallization and peak crystallization temperatures were obtained by differential thermal analysis (DTA, Setaram Labsys, Setaram Instrumentation, Caluire, France) of glass powders in air atmosphere from room temperature to 1000 °C at a heating rate of 5 K $min^{-1}$. Samples of glass powders weighing 50 mg were contained in an alumina crucible and the reference material was α-alumina powder.

The sintering/fluency behavior of the glass powders was investigated using a side-view hot-stage microscope (HSM) EM 201 equipped with image analysis system and 1750/15 Leica electrical furnace. The measurements were conducted in air with a heating rate of 5 K $min^{-1}$.

The coefficient of thermal expansion (CTE) of glasses and glass-ceramics was obtained from dilatometry measurements which were carried out on prismatic samples with a cross section of 4 mm × 5 mm (Bahr Thermo Analyze DIL 801 L, Hüllhorst, Germany; heating rate 5 K $min^{-1}$). The dilatometry measurements were made on a minimum of 3 samples from each composition and the standard deviation for the reported CTE values were in the range $\pm 0.1 \times 10^{-6}$ $K^{-1}$.

Rectangular bars with dimensions of 4 mm × 5 mm × 50 mm were prepared by uniaxial pressing (80 MPa). The as-obtained bars were firstly sintered at 850 °C for 1 h and then further heat treated at the same temperature for 500 h and 1000 h. A heating rate of 5 K $min^{-1}$ was used up to the set temperature. Synthesized glasses and glass-ceramics were evaluated according to the experimental protocols developed for testing the applicability of glass materials as sealants in SOFCs mentioned elsewhere [20–24]. The mean values and the standard deviations (SD) presented for CTE and bending-strength values were obtained from at least 3 and 10 different samples, respectively. The error values mentioned for DTA and HSM characteristic temperatures are based on instrumental errors in the determination of temperature which are ±3 °C for DTA and ±5 °C for HSM.

**Table 1 – Nominal batch compositions of the glasses (mol.%).**

| Glass | CaO | MgO | BaO | SrO | $Al_2O_3$ | $La_2O_3$ | $SiO_2$ | NiO |
|---|---|---|---|---|---|---|---|---|
| Sr/Ca = 3/6 | 15.00 | 25.02 | 0.56 | 7.50 | 1.25 | 1.25 | 48.60 | 0.85 |
| Sr/Ca = 5/4 | 9.98 | 24.96 | 0.59 | 12.49 | 1.25 | 1.25 | 48.60 | 0.88 |
| Sr/Ca = 7/2 | 4.99 | 24.93 | 0.61 | 17.46 | 1.25 | 1.25 | 48.59 | 0.92 |
| Sr/Ca = 9/0 | – | 24.92 | 0.63 | 22.43 | 1.24 | 1.25 | 48.58 | 0.95 |