

UDK: 666.112.3; 622.785

Effect of Sintering Parameters on the Densification, Microstructure, and Mechanical Properties of SrO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂-TiO₂ Based Glass Sealant

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Abstract:

In this study, sintering experiments were carried out on SrO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂-TiO₂ glass system with varying temperature, time and heating rates. The density of samples increases with the increase in temperature from 750 to 850°C. Thereafter, significant improvement in density is not noticed. The dwell time and heating rate have no marked impact on the improvement in density. From 850°C onwards, samples exhibit the peaks of crystalline phases confirmed by XRD. SEM images show the progressive increase in the compactness of microstructure with the reduction in porosity. The increase in HV with the increase in sintering temperature is attributed to the simultaneous increase in density. The highest hardness was obtained for the sample sintered within 850-950°C for 1h and a heating rate of 8°C/min. The Young's modulus is found to be of similar trend, like hardness. The CTE of annealed and sintered glass is 10.2×10^{-6} and $9.8 \times 10^{-6}/^{\circ}\text{C}$, respectively.

Keywords: Glass; Mechanical property; CTE.

1. Introduction

Solid oxide fuel cells (SOFC) are being increasingly used throughout the world as one of the clean energy generation resources [1-5]. Generally, planar type SOFC is preferred over contemporary tubular SOFC because of the higher power density and efficiency of the former [6,7]. Anode supported planar SOFC is usually operated within the temperature range of 600-800°C and is denoted as the intermediate temperature SOFC (IT-SOFC) [8-10]. In planar SOFC stack, to prevent the mixing of fuel (hydrogen or natural hydrocarbon gas) and oxidant (oxygen, air) as well as to inhibit the leakages of those gases, and to make an insulating layer between SOFC components, high temperature stable sealants are used [1-5]. There are various types of sealants available such as rigid sealants [4, 5, 11, 12], compressive sealants (metallic (silver, gold), mica based) [4,5,11-14], and compliant sealants (self-healing viscous glass, ceramic particle filled glass, and partially crystallized glass) [15-18]. Among them, the glass-ceramic based sealant is widely used because of its unique advantages of rigid bonding, thermal expansion compatibility with other fuel cell components, low-leak rate, thermomechanical, thermochemical stability, and also commercial availability [19, 20]. More importantly, there is enough scope for tuning the composition to tailor the properties of glass [9, 11]. In the SOFC stack, although the volume of sealant is relatively low compared to other

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fuel cell components, the role of the sealant is very significant, looking into the long life and reduction in the downtime of the SOFC stack.

Glass sealant is applied in the form of a paste or thin tape consisting of glass powder and an appropriate organic binder [11, 21-24]. To obtain a good sealing ability, it is essential for the glass powders to be sintered first, followed by flowing up to the outer edge of the stack, and subsequently crystallized. If significant crystallization occurs in the glass before sintering, there is enough chance of pore formation in the glass matrix, and the flow of the glass also gets inhibited due to the crystallization induced enhanced viscosity [25, 26]. Also, due to the presence of pores in the sealant, leak resistance is often found to be deteriorated [13]. Hence, it is important to study the sintering behaviour of glass powder for designing the heat treatment parameters for obtaining the optimum efficiency of the sealant.

In the past, a limited amount of study was carried out on the sintering of SrO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂-TiO₂ glass powder. Silva et al. studied the sintering and crystallization behaviour of the CaO-SrO-B₂O₃-TiO₂-SiO₂ glass powder compact. In their study, it is stated that the predominant crystallization mechanism is controlled by the surface in the above-cited glass system, and the growth of the crystalline layer is governed by the diffusion mechanism [24]. In case of the sintering of similar glass powder, the majority of the glass compositions exhibited a single-stage shrinkage behaviour, and TiO₂ added compositions showed higher sintering ability [24]. In another study, Reis et al. demonstrated that in the case of Ca-Sr-Zn-silicate glass system, the crystallization kinetics dominates over sintering for smaller particle size glass powder (< 20 µm). In contrast, relatively larger particle size powder (> 45µm) exhibited slow crystallization behaviour [23]. The study showed that smaller particle size glass powder showed rapid crystallization kinetics over sintering, leading to the formation of a porous seal [23]. It is also reported that the difference between the onset of crystallization temperature (T_x) and maximum sintering temperature (T_{MS}) is minimum for larger particle size (> 45µm) in comparison to that of smaller particle size glass powder (< 20 µm) [23].

Prado et al. demonstrated using polydispersed soda-lime-silica glass beads that concurrent crystallization impedes the densification of glass during the heat treatment process [28]. On the other hand, it is emphasized that glass powder of smaller particle size promotes densification during sintering [27]. In ceramic systems, finer powder generally facilitates more densification compared to the coarser powder due to the higher driving force associated with the former type of powder owing to its higher surface area [27]. Of course, viscous flow is the mechanism of densification for glass powder, whereas diffusion (grain boundary, lattice type) is the process of densification in the case of ceramic powder [28]. According to Kingery et al., the initial rate of shrinkage of the powder compact is inversely proportional to the particle size [28].

Prado et al. stated that glass powder compact is usually sintered at a temperature above the glass transition temperature (T_g), where the viscosity behaviour obeys the Vogel-Fulcher-Tamman (VFT) equation, i.e., viscosity decreases with the rise of temperature [26].

Regarding sintering, it is important to mention that some well-controlled sintering parameters, like appropriate heating rate, nucleation sites and smaller particle size, favour densification over crystallization of glass. The study also highlighted that a higher heating rate could even overcome concurrent crystallization [29].

Therefore, it can be intuitively stated that a synergistic combination of fine particle size and appropriate heating schedule, including sintering temperature, dwelling time [30] and heating rate, could help in obtaining dense glass compact with minimum crystallization.

If substantial crystallization occurs before densification, there is a great probability of forming many pores within the seal, which in turn is responsible for the leakage of fuel gases as hermetic sealing is impaired. In the open literature, a significant study is not available in the area of sintering for SrO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂-TiO₂ glass system. Hence, considering the crucial application and availability of limited technical data, studying the sintering behaviour of the above-cited SrO-based glass system is essential.

In our experiment, the strontium oxide based alumino-silicate glass system ($\text{SrO-CaO-ZnO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$) is chosen for experimental purposes. Such glass system is a potential sealant for planar SOFC application because of its low rate of interfacial reaction with metallic interconnect due to the precipitation of Sr_2SiO_4 and SrTiO_3 compounds and thermal expansion compatibility with remaining fuel cell components, which is evident in many scientific articles and reports [24, 31]. In this study, pellets made from fine glass powders were sintered at different temperatures, times and heating rates to standardize temperature-time-heating rate combinations for obtaining the dense glass seal. Further, we studied microstructural features, the room temperature basic mechanical properties (Young's modulus, hardness), and linear thermal expansion. In addition, the concomitant crystallization of glass powder was also investigated. A relatively fine glass powder was deliberately chosen as starting feedstock with an intuition that the fineness of the particle facilitates densification during sintering [25, 26].

2. Materials and Experimental Procedures

2.1 Raw materials

The starting raw materials, such as SrCO_3 , CaCO_3 , SiO_2 powders, were obtained from Loba Chemie Pvt. Ltd., India. SrCO_3 and CaCO_3 were used to obtain SrO and CaO , respectively, upon thermal decomposition of their respective carbonate compounds at higher temperatures (decomposition temperature of $\text{SrCO}_3 \approx 1000\text{-}1200^\circ\text{C}$ and $\text{CaCO}_3 \approx 650\text{-}765^\circ\text{C}$, respectively) [32-34]. Boric acid (H_3BO_3) powder (source of B_2O_3) was obtained from Fisher Scientific, India. Alumina (Al_2O_3) powder (Grade: CT 3000 LS SG) was obtained from Almatix Alumina Pvt. Limited, India. The ZnO powder was obtained from FINAR, India and TiO_2 powder was obtained from Loba Chemie Pvt. Ltd., India. The composition of $\text{SrO-CaO-ZnO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ glass system is similar to the G50 glass sealant developed by R. Brow et al. at the University of Missouri-Rolla, Rolla, USA, as reported in their research report [23, 27]. The mol% of the oxide ingredients and raw materials, along with their compositions including the purity, are provided in Table I.

2.2 Powder mixture preparation

The as-received oxides and carbonate powders of appropriate quantities were taken in a plastic jar and mixed for 72 h using an acetone medium in the presence of sintered alumina balls. The mixing time was kept longer to obtain uniformity in the mixing of all the ingredients as much as possible. After the completion of mixing, the wet mass was dried through the evaporation of acetone in ambient conditions and passed through ≈ 60 BSS sieve to remove coarse aggregates. The as-sieved powder mixture was used as feedstock for producing glass. The mole percentages and corresponding weight percentages of all the glass-forming ingredients are described in Table I.

2.3 Glass melting and frit preparation

The as-sieved powder mixture was kept inside a $\approx 99.7\%$ dense Al_2O_3 crucible and placed in an electric resistance heating furnace for melting purposes. The temperature for melting the batch was raised to 1550°C at the heating rate of $8^\circ\text{C}/\text{min}$ and dwelled at that temperature for 2h. The molten glass was quenched into ambient temperature water to form frits. The as-quenched frits were dried at 110°C for 24 h to evaporate the water, followed by rinsing with acetone. The dried frits were made into fine powder employing planetary milling.

Tab. I Percentages of ingredients and chemical composition of the raw materials.

Name of the oxide ingredients	(%) of ingredients		Starting raw materials	Purity of raw materials	Trace elements
	Mol.	Wt.			
SrO	25.48	36.48	SrCO ₃	98% (Min.)	Fe = 0.002% (Max.), Ni = 0.002% (Max.), Cu = 0.002% (Max.), Pb = 0.002% (max.), Chloride (Cl) = 0.02% (max.), Phosphate (PO ₄) = 0.005% (max.),
CaO	25.48	19.74	CaCO ₃	98% (Min.)	Chloride (Cl) = 0.025% (max.), Sulphate (SO ₄) = 0.3% (max.), substance insoluble in acetic acid = 0.2% (max.)
ZnO	3.92	4.40	ZnO	99% (min.)	Fe = 0.005% (Max.), Chloride = 0.02% (max.), phosphate (SO ₄) = 0.005% (max.), Chloride (Cl) = 0.025% (max.), Pb = 0.05% (max.), Carbonate (CO ₃) = 0.5% (max.)
Al ₂ O ₃	1.96	2.75	Al ₂ O ₃	99.8%	Na ₂ O = 0.03%, Fe ₂ O ₃ = 0.015%, SiO ₂ = 0.015%, MgO = 0.040%, CaO = 0.015%
B ₂ O ₃	1.96	1.88	H ₃ BO ₃	99.5% (min.)	AS = 0.0001% (Max.), Chloride (Cl) = 0.01% (max.), Sulphate (SO ₄) = 0.04% (max.), Pb = 0.002% (max.)
SiO ₂	39.2	32.54	SiO ₂	Extra pure	-
TiO ₂	2.0	2.21	TiO ₂	99% (min.)	Fe = 0.02% (Max.), As = 0.0003% (Max.), Sb = 0.005% (Max.), Acid soluble matter = 0.5% (max.), Water soluble matter = 0.5% (max.)

[#] According to the manufacturer's certificate of analysis

2.4 Pelletization, debinding and sintering

The fine glass powder was mixed with 1.5wt% QPAC-40 binder (a polycarbonate based organic compound) followed by compaction at ≈ 120 MPa to make ≈ 10 mm diameter and ≈ 5 mm thickness circular pellets. The QPAC-40 binder was used as it does not produce any burn-out residue in the sintered glass. The green pellets were sintered at the temperature range of 750-950°C at a regular temperature interval of 50°C and dwelled for different durations. The summary of sintering temperature, dwell times, and heating rates, along with the respective sample identification codes, are depicted in Table II. It is to be mentioned that the different temperatures, dwell time, and heating rate were considered mainly for studying

the sintering of glass powder compacts as the above-cited parameters have a good role in designing glass-ceramic sealant for SOFC stack applications.

Tab. II Sample details, sintering parameters and properties.

Sample code	Sintering parameters	Bulk density (g/cc)	E (GPa)	HV _{0.3} (GPa)
SCZ-A	750°C / 1h / 8°C/min	3.07	-	1.1 ± 0.2
SCZ-B	800°C / 1h / 8°C/min	3.22	-	3.3 ± 0.9
SCZ-C	850°C / 1h / 8°C/min	3.30	113 ± 10	7 ± 0.2
SCZ-D	900°C / 1h / 8°C/min	3.30	119 ± 9	6.8 ± 0.5
SCZ-E	950°C / 1h / 8°C/min	3.30	117 ± 7	6.5 ± 0.5
SCZ-F	950°C / 2h / 8°C/min	3.15	111 ± 16	6.0 ± 0.5
SCZ-G	950°C / 1h / 2°C/min	3.19	96 ± 4.5	5.2 ± 0.7
SCZ-H	950°C / 1h / 15°C/min	3.21	99 ± 9	6.5 ± 0.7

2.5 Characterization techniques

The particle size distribution (PSD) of the glass powder was measured based on the laser scattering method using a particle size analyzer (Mastersizer 2000 Ver.5.60, Malvern Instruments Ltd., Malvern, UK). The glass transition temperature (T_g), onset crystallization temperature (T_x), and peak crystallization temperature (T_p) was determined using the glass powder sample with the help of differential scanning calorimetric (DSC) method in a simultaneous thermal analyzer (NETZSCH STA 449F3) [35].

The bulk density of the sintered samples was determined with the help of the water displacement method using Archimedes' principle [36]. The crystalline phases present in the sintered samples were identified through the analysis of X-ray diffraction (XRD) patterns recorded using a powder X-ray diffractometer (Rigaku, Japan). For microstructural analysis, the sintered samples were sectioned and finally polished using 1 μ m diamond particle suspension. Subsequently, the samples were etched using 5wt% HF acid solution for 5 min. The etched surfaces of the sintered specimens were examined using secondary electron (SE) imaging with the help of a field emission scanning electron microscope (FESEM, Carl Zeiss, Gemini 500).

Young's modulus (E) of sintered samples was determined from load-displacement plots generated through the nanoindentation test (Micromaterials, USA) using load control mode under a constant load of 100 mN, such that the maximum depth of penetration was ≈ 1.0 μ m. It is to be noted that an average value from ten indentations, along with the standard deviation for each sample, is presented here. Vickers hardness was measured according to the standard ASTM C1327-15 using a microhardness tester (Model: UHL VMHT, Water Uhl Technische Mikroskopie GmbH, Germany) under a load of 2.94 N (0.3 kgf) [37]. The average hardness value of seven indents is reported in this study. The linear thermal expansion of the annealed glass sample and sintered sample (SCZ-E) was recorded with the help of a thermo-mechanical analyzer (TMA, Q400, TA Instruments, USA).

3. Results and Discussion

3.1. Particle size distribution

The particle size distribution (PSD) of planetary milled glass powder is shown in Fig. 1. There are two peaks in the PSD curve, as indicated by arrow marks in Fig. 1. However, the intensity of peak-2 is negligible compared to that of peak-1. The PSD curve reveals that the median particle size (D_{50}) of the powder is ≈ 5.2 μ m, whereas D_{10} and D_{90} are ≈ 1.5 μ m and $\approx$

21.6 μm , respectively. Therefore, it can be stated that the glass powder consists of fine particles, and mostly monomodal type has a narrow size range.

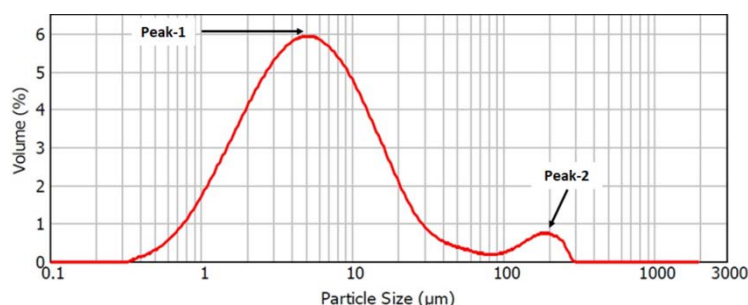


Fig. 1. Particle size distribution of planetary milled glass powder.

3.2. Differential scanning calorimetric study

The DSC curve for the glass sample is provided in Fig. 2, which shows a small step in the DSC signal at 635°C corresponding to T_g . In addition, two distinct exothermic peaks are noticed, indicated by Peak 1 and Peak 2, signifying the transformation of glass-to-crystals of two different temperature regimes. In the case of peak 1, T_x and T_p are 825°C and 845°C respectively; whereas, T_x and T_p corresponding to peak 2 are 900°C and 935°C, respectively. It is noticed from Fig. 2 that the area under the second peak is significantly higher than that of the first peak, elucidating that energy released (or enthalpy of crystallization) during the glass-to-crystal transformation is higher in the case of peak 2 compared to that of peak 1. In the case of a similar type of glass (G50) reported by Brow et al., the T_g and T_x are 700°C and 890°C [27], respectively, slightly differing from our results. Such deviation can be attributed to the origin of raw materials and their impurity content, experimental parameters, and the type of crucible used for glass melting. The dense Al_2O_3 crucible was used for glass melting in our experiment, whereas the platinum crucible was used in the investigation carried out by the R. Brow group [23, 27].

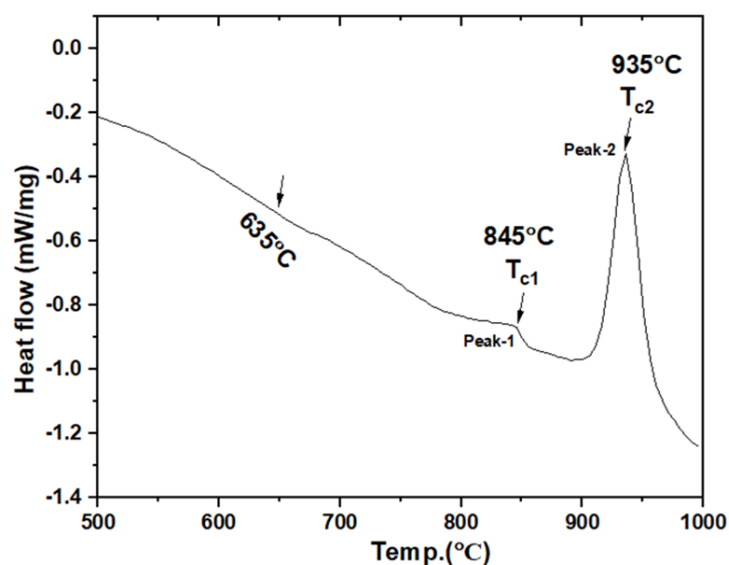


Fig. 2. Differential scanning calorimetric plot for glass powder.

3.4. Bulk density

Table II shows that for samples SCZ-A to SCZ-C, with the increase in sintering temperature from 750 to 850°C with 50°C intervals, the density increased by $\approx 4.9\%$ and $\approx 2.5\%$, respectively. Further, for samples SCZ-D and SCZ-E sintered at 900 and 950°C, respectively, the density remains almost constant, i.e. 3.30 g.cm^{-3} . In the case of SCZ-F, sintered at 950°C for 2h, the density decreased by $\approx 4.5\%$ compared to that of SCZ-E, indicating that longer dwell time did not favour an increase in density. On the other side, SCZ-G (sintered under the slowest heating rate) and SCZ-H (sintered under the fastest heating rate) exhibit almost similar density ($\approx 3.20 \text{ g/cc}$), but both demonstrated slightly lower density by $\approx 3\%$ than that of sample SCZ-E sintered under intermediate heating rate (8°C/min). Such experimental results show that the heating rate did not have a remarkable influence on the change in density.

In comparison to the density value of SCZ-A to SCZ-C, it can be stated that during the increase in temperature, there is a decrease in porosity with concomitant shrinkage through the mass transfer by the flow mechanism. For SCZ-D and SCZ-E, an increase in density is not noticed, which is due to the fact that the low amount of isolated remnant pores in the compact at the final stage of sintering. Intuitively it can be stated that such low porosity could not provide a sufficient driving force for further improvement in density.

On comparison between SCZ-E and SCZ-F, it is noticed that the density of the later sample is decreased by $\approx 4.50\%$, which can be attributed to the possible slight evaporation of glass because of the longer holding time at the target sintering temperature (950°C). The slowest and fastest heating rate did not play a significant role w.r.t. the improvement in density, as observed for SCZ-G and SCZ-H. Here, the effect of temperature dominates over the ramp rate of heating, signifying that the effect of thermal energy is more dominant than the time of exposure of the sample along the heating span. Under the present experimental conditions, the heating rate 8°C/min appears to be the most effective looking into improvement in the density.

The mechanism of densification in the case of glass powder can be explained accordingly. During the densification of a glass powder compact, when two particles are in contact at the initial stage, a negative pressure exists at the neck region, having a small negative radius of curvature compared with the particles' surface [29]. Such a pressure difference acts as a driving force for the transport of matter into the pore region through viscous flow, under the influence of thermal energy. After a certain duration of sintering, the simultaneous crystallization leads to the entrapment of pores within the crystalline regime and most likely inhibits further density improvement. Such residual pores are generally known as closed pores and are difficult to eliminate from the densified body through pressureless sintering [25, 29]. In addition, the formation of crystalline regions in the specimen also inhibits densification [26].

4.5. X-ray diffraction pattern

The X-ray diffraction patterns of glass powder and sintered samples are depicted in Fig.3(i-ix). The X-ray diffraction pattern (XRD) of glass powder (Fig.3(i)) mainly consists of diffuse humps, confirming the non-crystalline characteristics of glass. The sample sintered at 750°C exhibited similar characteristics to that of glass powder, indicating crystallization did not get initiated at this temperature. However, with a further increase in sintering temperature to 800 to 950°C (sintered for 1h), several crystalline phases occurred, which is confirmed by the appearance of signature peaks in the XRD patterns (shown in Fig.3(ii - viii)). No distinct shift in peak position is noticed with the rise of temperature as well as with heating time or heating rate. Similar crystalline phases are noticed at identical peak positions in the sample sintered at 950°C for 2h (Fig.3(ix)). The crystalline phases formed upon sintering are $\text{Sr}_2\text{Al}_2\text{O}_7$

(2022 International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) number 00-038-1333), Sr_2SiO_4 (ICDD PDF number 00-010-0034), $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ (ICDD PDF number 00-035-0745), and SrTiO_3 (ICDD PDF number 04-014-1850). Interestingly, identical crystalline phases are observed at temperatures between 800–950°.

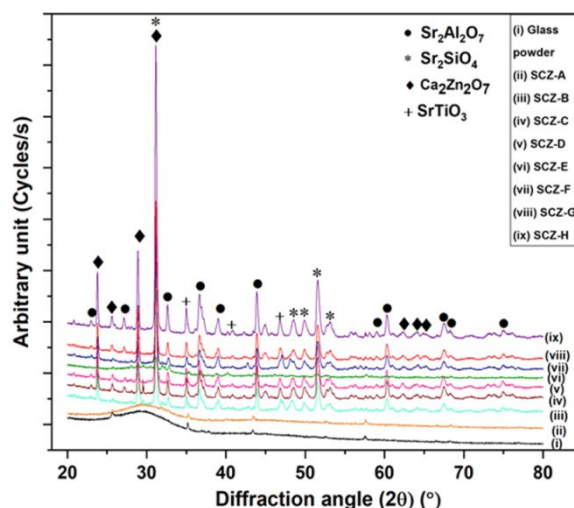


Fig. 3. X-ray diffraction patterns of: (i) glass powder, (ii) SCZ-A, (iii) SCZ-B, (iv) SCZ-C, (v) SCZ-D, (vi) SCZ-E, (vii) SCZ-F, (viii) SCZ-G, and (ix) SCZ-H.

3.6. Scanning electron microscopic examination

The secondary electron (SE) scanning electron micrographs (SEM) are shown in Fig. 4(a-c) for sintered specimens SCZ-C, SCZ-D, and SCZ-E, respectively, to illustrate the effect of temperatures on microstructural features. To demonstrate the effect of time, a comparison has been made between SCZ-E and SCZ-F (sintered at the highest temperature, i.e. 950°C), having different time durations, i.e. 1h and 2h, respectively. SEM image of SCZ-F is depicted in Fig. 4(d).

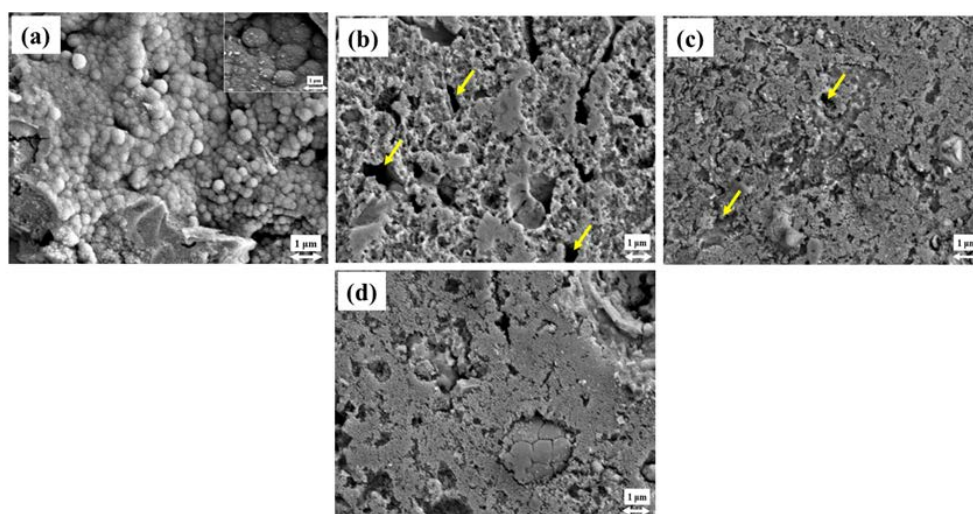


Fig. 4. SEM images of: (a) SCZ-C, (b) SCZ-D, (c) SCZ-E, and (d) SCZ-F. Arrow mark indicates pores.

The sample sintered at 850°C shows the fusing of glass particles, and evidence of neck growth is found, as observed in Fig.4 (a) and inset in Fig. 5(a), respectively, indicating that sintering got initiated at this temperature. Fig. 4(b) (for SCZ-D) demonstrates relatively more densification than that of SCZ-C, which is obviously due to more mass transfer because of more thermal energy imparted at a higher temperature. Of course, some closed pores are noticed, as indicated by the arrow marks in Fig. 4(b). In the case of SCZ-E, a more compact and less porous microstructure is noticed due to a higher reduction in closed pores, but those were not fully eliminated. A scatter appearance of pores is still noticed in the micrograph. In the case of SCZ-F, a more or less similar microstructure is detected, and interfacial boundaries are observed between newly formed grains or crystalline regions as shown by arrow marks in Fig. 4 (d), and evidence of a few pores is also found. The micrographs of SCZ-G and SCZ-H are not described here as their microstructural features do not exhibit any significant difference compared to that of SCZ-F.

3.7. Young's modulus

The room temperature Young's modulus (E) of the samples SCZ-C to SCZ-E (sintered within the temperature range of 850-950°C), respectively, is almost similar, i.e., the values are in the range of 113-119 GPa. Such a trend can be corroborated by almost similar densities of those samples. In fact, SCZ-F also shows more or less equal value or marginally lower (≈ 111 GPa), indicating that soaking time at identical sintering temperature does not substantially influence the E value under the present experimental setup.

3.8. Hardness and characteristics of indentation crack

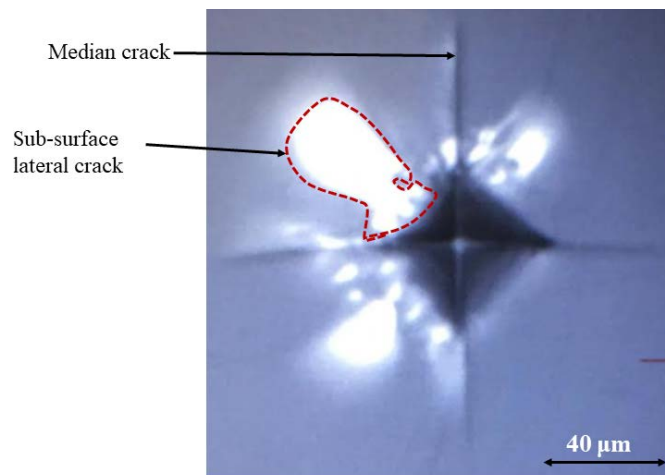


Fig.5. Vickers indentation imprint of as-cast glass

Fig. 5. Vickers indentation imprint of as-cast glass.

Table II depicts the microhardness ($HV_{0.3}$) values of sintered samples. On comparison, it is found that SCZ-B shows improved hardness by $\approx 200\%$ to that of SCZ-A, whereas SCZ-C shows a higher hardness than that of SCZ-B by $\approx 112\%$. Such a substantial increase in hardness is mainly attributed to the significant increase in density with the increase in sintering temperature. In the case of SCZ-D and SCZ-E, the hardness value of both samples is almost similar, which can be attributed to their more or less equivalent density. On comparison between SCZ-E and SCZ-F, it is found that SCZ-F exhibited a lower density than that of SCZ-E by $\approx 7.7\%$, indicating that more dwelling time is responsible for the reduction

in hardness, which is further supported by their density difference also (shown in Table II). Additionally, the leftover void regions believed to be formed by slight evaporation of the glassy phase during longer dwelling time in the case of SCZ-F caused the reduction in hardness. SCZ-G demonstrated lower hardness by $\approx 20\%$ than that of SCZ-E, signifying that a low heating rate ($2^\circ\text{C}/\text{min}$) does not favour hardness improvement as it did not favour improvement in density, whereas SCZ-H exhibits more or less similar hardness to that of SCZ-E.

On examination of the indentation imprint of the polished glass sample (Fig. 5), it is found that median cracks emanate from the corners of the indentation. In addition, lateral sub-surface cracks are observed, as marked by a brown dotted area in Fig. 5. Such features show the extreme brittleness of glass.

3.9. Linear thermal expansion

The thermal expansion of materials occurs due to the anharmonic vibration of atoms. Such anharmonicity originates as the repulsive and attractive forces between atoms are not symmetrical, which can be visualized from the Condon-Morse potential energy diagram described elsewhere [36, 37]. At a temperature above 0 K, atoms have some thermal motion and vibrate with respect to their equilibrium position. As the temperature increases further, there is a progressive increase in the amplitude of the vibration of atoms. Due to the anharmonicity in atomic vibration, there is an increase in the interatomic distance as a function of temperature, eventually leading to the expansion of the substance. Additionally, variation in bond angle without any significant change in bond length is another contributing factor to the thermal expansion of glass, particularly [38].

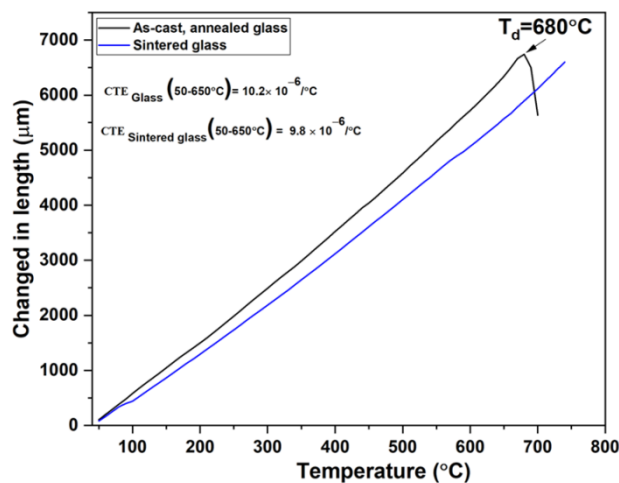


Fig. 6. Linear expansion versus temperature plot for glass and sintered glass.

The linear thermal expansion plots for glass and sintered glass specimens are depicted in Fig. 6. The plot in the case of glass is trending down from a temperature of $\approx 680^\circ\text{C}$, which is known as the dilatometric softening point (T_d). However, the linear expansion plot of sintered glass compact does not exhibit such a downward trend even up to 850°C . Such a phenomenon can be corroborated to the concurrent crystallization or ceramization that has taken place within the glass matrix during sintering (evident from XRD patterns). The presence of such crystals improved the refractoriness of the sample and shifted the softening point beyond 850°C . The marginal decrease in the linear expansion in the case of sintered glass could be due to the formation of strong bonds in the crystalline structure. The crystalline phase formed due to the rearrangement of atoms in a regular pattern from the non-crystalline

structure of glass during the heat treatment process through nucleation and growth mechanism [39-42]. Here, the surface of the particles acts as the nucleation and growth centre, and TiO_2 , an effective nucleating agent, facilitates the crystallization process [24, 39-42]. The coefficient of thermal expansion (CTE) was derived from the slope of the plot in the temperature range of 50 - 650°C, which is 10.2×10^{-6} and $9.8 \times 10^{-6}/^\circ\text{C}$ for glass and sintered glass, respectively, and the values are close to the CTE of other SOFC components like YSZ, Ni-YSZ, and metallic interconnects [6, 43, 44]. The difference in CTE between glass and sintered glass is numerically insignificant.

4. Conclusion

Based on the experimental results and their careful analysis, the following points are summarized:

- (i) The effect of temperature on the improvement in density is prominent. However, the heating rate and dwell time do not have much influence on the variation in density. Increase in density has occurred through the mass transfer through the temperature-induced viscous flow mechanism.
- (ii) X-ray diffraction patterns revealed various crystalline phases, namely $\text{Sr}_2\text{Al}_2\text{O}_7$, Sr_2SiO_4 , $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and SrTiO_3 . The onset of crystallization was noticed from 800°C.
- (iii) The hardness values are drastically increased up to the samples sintered at 850°C. However, a large hardness value was achieved within the temperature range of 850-950°C. Sample sintered at 950°C with 2h dwell time demonstrated relatively lower hardness, possibly due to an evaporation-induced lower density of the glass sample (i.e. SCZ-F). Young's modulus also exhibits an almost similar trend to that of hardness.
- (iv) Scanning electron micrograph reveals that an increase in sintering temperature favour progressive compactness of microstructure and reduction in porosity.
- (v) The linear thermal expansion of sintered glass is marginally lower than that of glass within the temperature range of 50-650°C. CTE values derived from linear expansion plot for both samples show those CTEs are close to each other.

Acknowledgments

The authors would like to thank Director-ARC International for his kind permission to publish this work. We express our gratitude to Dr. Buchi Suresh, Dr. P. Suresh Babu, Dr. Balaji Padya (Scientists) for extending their kind support to carry out the particle size analysis, Young's modulus measurement by nanoindentation and DSC experiment, respectively. Our thanks also go to Mrs. B.V. Shalini, and Mr. R. Anbarasu (Technical Officers, CACM) for their technical support in carrying out the glass melting activity.

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Сажетак: У овој студији, експерименти синтеровања су спроведени на SrO-CaO-ZnO-Al₂O₃-B₂O₃-SiO₂-TiO₂ стакленом систему са различитим температурама, временом и брзинама загревања. Густина узорака расте са порастом температуре од 750 до 850°C. Након тога се не примећује значајно повећање густине. Време задржавања и брзина загревања немају значајан утицај на побољшање густине. Од 850°C надаље, узорци показују никове кристалних фаза потврђене рендгеном. СЕМ слике показују прогресивно повећање компактности микроструктуре са смањењем порозности. Повећање HV са повећањем температуре синтеровања приписује се истовременом повећању густине. Највећа тврдоћа је добијена за узорак синтерован на 850-950°C у трајању од 1 сата и брзином загревања од 8°C/мин. Утврђено је да је Јунгов модул сличног тренда, попут тврдоће. ЦТЕ жареног и синтерованог стакла је $10,2 \times 10^{-6}$ и $9,8 \times 10^{-6}/^{\circ}\text{C}$, респективно.

Кључне речи: стакло; механичка својства; ЦТЕ.

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