Optimization of the synthesis route of a barium boron aluminosilicate sealing glass for SOFC applications

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A B S T R A C T

A barium boron aluminosilicate sealing glass for IT-SOFC or SOFC applications was synthesized using different routes. Notably, sol-gel and solid state processes were used in order to obtain homogeneous glasses at 1100–1300 °C. Sol-gel processes consist in a soft chemistry route allowing a better homogeneity between cationic precursors in the mixture and a better reactivity of the material. The influence of the process and of the glass processing temperature on the thermo-mechanical properties of the glasses were investigated after different heat treatments in air atmosphere, i.e. glass processing, sealing (850 °C-2 h) and ageing (800 °C-100 h) procedures. It had been observed that the grain size of the glass powder (obtained after the glass processing and used for the sealing operation) is determining in order to manage the sealing procedure. Some large pores were formed during the devitrification step of the glass made by solid state route while glass sealants synthesized by the sol-gel route even at 1100 °C remained suitable for SOFC applications after thermal treatments, which proved that the sol-gel process is useful to decrease the glass processing temperature.

1. Introduction

SOFC or IT-SOFC (Intermediate Temperature Solid Oxide Fuel Cell) systems allow a direct conversion of chemical energy of a fuel into electrical energy and supplementary heat produced can be exploited. Stacks of individual cells connected in series have a great potential for power generation either in mobile or stationary applications and must work in the temperature range 500–1000 °C [1,2]. One of the challenges of this emerging conversion technology concerns the development of a sealant material ensuring the gas-tightness of cathodic and anodic compartments of the cells. The most important physico-chemical properties of the sealant material are high temperature stability, electrical insulation (10^4 Ω cm), stable coefficient of thermal expansion (CTE) close to other cells components ($10–13{\cdot}10^{-6}$ K^{-1}), chemical inertia in reducing and oxidizing atmospheres and a sufficient plasticity at the joining temperature [3].

Various sealants materials have been investigated for this application, such as viscous and rigid glasses, glass-ceramics and cements [4,5]. Glass-ceramics are great candidates because they are flexible materials, i.e. a wide range of chemical compounds can be mixed in order to match with properties required for cells operation [4–7].

Among the glass-ceramics, a lot of investigations had been realized on barium boron aluminosilicate glass-ceramics due to the fact that these materials have CTE close to the CTE of the other cells components (steel interconnector and ceramic electrolyte) [8–17]. During the sealing process, a partial crystallization of the primary glasses occurs with the formation of various barium silicate crystals with high CTE varying from 9 to $17{\cdot}10^{-6}$ K^{-1} [4,8–10]. Increasing BaO content and B_2O_3/SiO_2 ratio in that glasses allowed an increase of the CTE [11]. The addition of B_2O_3 generally produces a decrease of viscosity, a delay in the crystallization step, which leads to a greater wettability of the glasses on cells components. Other phases can be promoted or inhibited with adding different chemical compounds. For instance, small additions of CaO, MgO, Y_2O_3, La_2O_3 and ZrO_2 resulted in the formation of various crystals during devitrification process. Some of these crystals, like monocelsian $BaAl_2Si_2O_8$, have a low CTE and could cause a decrease of the CTE of glasses leading to a CTE mismatch with other cell components [4,10]. Barium boron aluminosilicate G18 glass developed at PNNL (Pacific Northwest National Laboratory, USA) showed the presence of this phase after only 1 h at 750 or 850 °C and a decrease of the CTE of 15% after 168 h under SOFC operating conditions [12]. The effect of Al_2O_3 content in barium boron aluminosilicate glasses had also been investigated [13]. It had been proved that Al_2O_3 improves the crystallization temperature of these glasses but it promotes $BaAl_2Si_2O_8$ formation since at least 2% Al_2O_3 are contained in the materials [13,14]. Another problem of the

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use of barium aluminosilicate glass-ceramics corresponds to the formation of $BaCrO_4$ crystalline phase (high CTE potentially leading to cracks) at the interface between the glasses and the metallic interconnector [7,15–18]. However, promising performances had been obtained on short-term or on mid-term operations in air (up to 1500 h in dual atmosphere with no delamination [19]), in dual atmosphere (no delamination after 750 h [20]) or in real testing conditions with thermal cycles for SOFC applications [21].

In our previous works, we had developed a new sol-gel route to synthesize barium (boron) aluminosilicate glass sealants in order to process these glasses at a lower temperature than using a solid-state route and to improve the performance of these glasses for SOFC applications [22–26]. Indeed, many studies showed that the use of gel mixture could decrease the temperature of glass formation until 200 K below (possibly more) those required when using conventional batch material [27–29]. By this process, the reduction of the process temperature is possible due to a better homogeneity of the cationic salts mixture, which could induce better material properties and increase lifetime. At 1300 °C, barium aluminosilicate glasses still contained crystals. With the adding of B_2O_3, MgO and/or CaO, amorphous and homogeneous BBXAS (BaO-B_2O_3-Al_2O_3-SiO_2 with X=CaO and/or MgO) glasses were obtained at the same temperature [22–24]. Four glass-ceramic sealants, with a T_g between 596 and 626 °C, showed adequate electrical insulation after a sealing procedure and stable CTE and microstructure after sealing and ageing operation (800 °C-100 h) in air atmosphere. Furthermore, any reaction product at the steel interconnector-glass interface was observed and no hexacelsian or monocelsian crystals were identified in the formed glass-ceramic seals [24]. However, only the CM2 glass (chemical composition: 36%BaO- 2.6%Al_2O_3-10.3%B_2O_3-10.3%MgO- 10.3% CaO- 30.7%SiO_2) allowed preserving the gas-tightness of steel-glass-steel assemblies thermally treated at 700 °C or at 800 °C during 1000 h in air and in H_2/H_2O atmospheres [25,26]. Using CM2 glass as sealant material, a promising stable electrical performance of a commercial SOFC was obtained (low reduction of the open circuit voltage) during ~2000 h at 800 °C under operating conditions with methane as fuel in cathodic compartment [30].

In this study, glasses with similar chemical composition of CM2 material were synthesized using sol-gel and solid-state processes at 1300 °C in order to confirm the benefits of the sol-gel process (lower processing temperature, better performance due to homogeneity). After processing, the glasses were crushed into fine grains to form a glass paste to facilitate the sealing procedure. The influence of the grain size after glass processing by sol-gel route was observed in order to better the use of these glasses in SOFC applications. Finally, a glass had also been processed at 1100 °C in order to try to decrease the processing temperature. Thermo-physical properties of the glasses as-formed were evaluated. Microstructure and thermomechanical properties of the glass-ceramics after a sealing and an ageing procedure were investigated to determine the better synthesis procedure for an SOFC application at 700–800 °C.

2. Material and methods

2.1. Synthesis routes

4 glasses with the same theoretical chemical composition of the promising CM2 material were prepared (Table 1). 3 glasses were synthesized using the sol-gel route previously described with a final processing heat treatment at 1300 °C during 3 h for SG1 and SG2 glasses and at 1100 °C during 1 h for SG3 glass [23,24]. Concerning the glass prepared by solid-state process, nearly-pure commercial powders $BaCO_3$, SiO_2, MgO, CaO and B_2O_3 (325 mesh, purity > 99,5%) were mixed together and heated at 1300 °C during 3 h. In this case, $BaCO_3$ powder was preferred to BaO powder to avoid any influence of residual impurities contained into BaO powders on the final glass chemical composition and the glass properties. All the glasses were ground using a planetary mill (agate balls and cup) at 400 rpm to obtain powders. Same grinding duration was used in order to obtain similar grain size except for SG1 glass (Table 1), which was already characterized in previous works [24,26].

Table 1
Description of the procedure fused to synthesize the glasses / glass powders.

Sample	Process	Processing treatment (°C)	Grinding duration @ 400 rpm
SG1	Sol-Gel	1300 – 3 h	5 h
SG2	Sol-Gel	1300 – 3 h	15 h
SG3	Sol-Gel	1100 – 1 h	15 h
SS1	Solid-state	1300 – 3 h	15 h

2.2. Characterization methods

After the glass processing and the grinding step, grains sizes were determined by a laser diffraction method, using a Beckman coulter LS particle size analyzer.

Thermo-physical properties of the glass powders were analyzed by using a Netzsch DSC 404. Scans were recorded from room temperature to 1100 °C at 10 K min^{-1}. T_g (transition temperature), T_X (onset crystallization temperature) and T_C (maximum crystallization temperature) of each glass were recorded (errors~ ± 5 °C).

Hot-stage microscopy measurements (HSM) were performed using a Hesse Instrument EMI1 equipment, which is composed of a CCD camera and a heat controlled furnace. Each glass powder was pressed into a pellet (~3 mm thick×3 mm Ø) and samples were heated at 10 K min^{-1} from room temperature to 1100 °C on standard platinum substrate. According to the norm DIN 51730 1998-04 (Testing of solid fuels - Determination of fusibility of fuel ash), sample morphologies and contact angles were determined by a computer program to calculate, T_S (softening), T_{SP} (spherical), T_{HB} (half-ball) and T_F (flow) of glass sample. Three pellets of each glass were analyzed in order to have a representative average of the results.

In order to investigate the evolution of crystalline phases and of the thermomechanical properties after thermal treatments, each glass powder was pressed into pellets (~2 mm thick×6 mm Ø). These pellets were heated during 2 h at 850 °C (heating rate 2 K min^{-1}) in order to simulate sealing conditions. After this treatment, some of these pellets were also heated (heating rate 2 K min^{-1}) during 10 h at 800 °C to simulate SOFC operating conditions (also called “ageing”). The crystalline structure of glass-ceramic pellets was analyzed using XRD (X-Ray Diffraction) technique after each thermal treatment. XRD equipment was a Brucker AXS D4 Endeavor. Scans were recorded between 10° and 100 ° operating in Bragg-Brentano (θ–2θ) mode. Measurements of CTE as a function of temperature were carried out on glass pellets before and after thermal treatments using a dilatometer with a sensor Setsys Evolution TMA. CTE values were calculated from 200 °C to 550 °C under air atmosphere; three pellets of each glass were characterized. Relative errors of the calculations were in the range ± 10%. Scans were recorded from room temperature to 1100 °C at 10 K min^{-1}. The samples were also analyzed using a SEM (Scanning Electron Microscope) model JEOL JSM 6700F.

3. Results

After the glass processing at 1100 or 1300 °C, all the materials were amorphous. No diffraction pattern was detected using XRD (Fig. 1a), no crystals were observed and no phase separation was detected using SEM (Fig. 1b). So, all the glasses were homogeneous. Few other melting tests (not presented here) performed at lower temperature for glasses made with conventional or sol-gel routes, respectively at

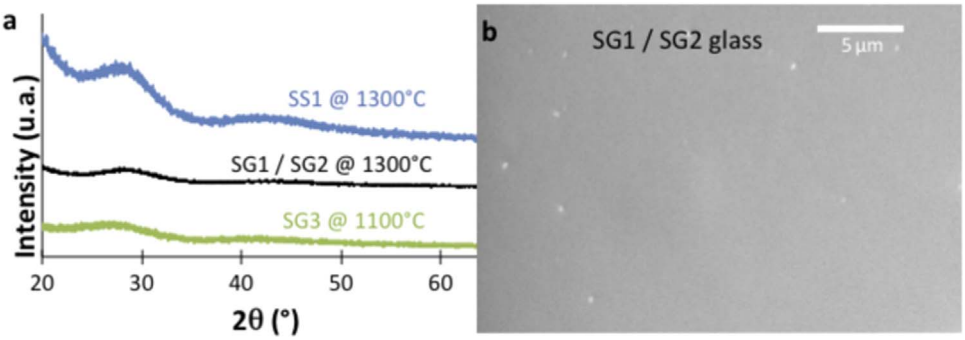

Fig. 1. a) XRD pattern of SS1, SG1/SG2 and SG3 glasses after glass processing, b) SEM image of SG1/SG2 glass.

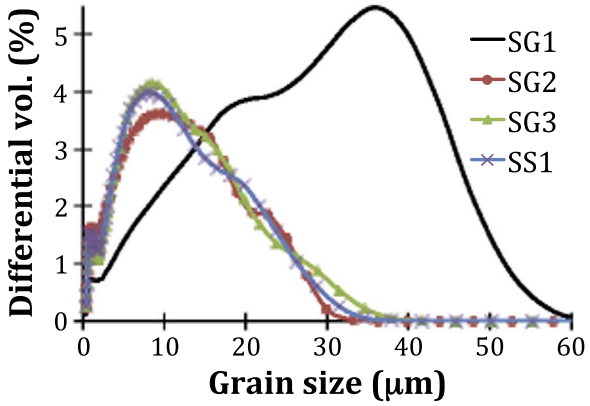

Fig. 2. Grain size distribution of the glasses after grinding operation.

1100 °C or 1000 °C showed that crystals were present in the formed glass leading to inhomogeneous systems. After the grinding operation, all the formed glass powders were polydisperse (Fig. 2). The median grain size in volume for SG2, SG3 and SS1 glasses was in the range 6–6.5 µm with grains smaller than 40 µm. Although the median grain size for SG1 is higher (17.5 µm), all the gains were smaller than 60 µm, which was suitable in order to seal SOFC components.

The T_g and T_x values of the four glasses are respectively close to 580–600 °C and 700–720 °C (Table 2). Considering the error on the measurements (± 5 °C), the differences appeared negligible. On the other hand, T_C of SG1 glass was 30–40 °C higher than T_C of other glasses, which proves that grain size has a little influence on the crystallization process.

The HSM software could not calculate T_{SP} values for all the glass samples synthesized by sol-gel process. A hypothesis is that the formation of crystals may inhibit the evolution trough a spherical profile by mechanical strain. By contrast, temperatures T_S, T_{HB} and T_F were determined at a reasonable precision for all glasses (± 5 °C except ± 10 °C for SS1 glass) and were considered as more reliable data. The thermal behavior of the glass samples synthesized by solid-state process was different from the others during HSM experiments (Fig. 3). After an initial sintering from 610 to 670 °C, an important increase of the volume, area and height of these samples occurred at ~760 °C while the profile of the glass samples made by sol-gel process was not really changed. Above 890 °C, all the glass samples had again a similar profile (from T_{HB} to T_F).

T_S of SG1 glass was nearly 200 °C lower than T_S of SG2 and SG3 glasses. So, the smaller grain sizes of SG2 and SG3 glass samples have an important effect on the thermal behavior of the sample above T_g. It is supposed that a greater specific energy of these powders increases the crystallization rate close to 700 °C (in particular at the surface), which preserves the profile of the glass samples during heating in HSM experiments and delay the softening. T_S of the sample synthesized by solid state route strongly depends on the brutal increase of the volume of the glass samples during heating procedure and could not be compared to T_S obtained for the other glasses.

T_{HB} of sol-gel glasses are generally high because of the probable accelerated formation of crystals, which slows the deformation of glass samples during heat treatment (Table 2). Changes in initial grain sizes and temperature processing appeared to have a weaker impact on T_{HB}, which could be explained. The formed crystals begin to melt at the same temperature in glass samples. T_{HB} of the SS1 glass is lower than those of the other glasses. In fact, during the heating from 770 to 900 °C, crystallization kinetics had probably been slowed by the energy released in the strong increase of the samples volume.

After the heat treatment of glass pellets at 850 °C during 2 h simulating a sealing operation, the profile of the formed glass-ceramics issued from the sol-gel process remained similar (Fig. 4b-d). By contrast, the formed glass-ceramics issued from SS1 glass were more voluminous with the presence of large pores (Fig. 4e and f).

XRD technique was used to identify the crystalline phases in the four materials (Fig. 5). The same crystalline phases were formed in glass-ceramics with nearly similar diffraction pattern. A monoclinic $Ba_2MgSi_2O_7$ phase, whose crystal structure has been recently reported, (calculated by Rietveld analysis assuming that $Ba_2MgSi_2O_7$ was isostructural to $Ba_2CoSi_2O_7$) is the major phase [10,31]. According to the PDF (Powder diffraction files) from ICCD (International Centre for Diffraction Data), further diffraction peaks could also be attributed to $MgSiO_3$, several barium calcium silicates or barium silicates, which could be present as minor phases (diffraction pattern of some of these phases are very similar to the monoclinic $Ba_2MgSi_2O_7$ pattern).

Various crystals were present and microstructural observations allowed to confirm it (Fig. 6). These crystals were generally anisotropic with edges in the range 1–10 µm in the formed glass-ceramics (the crystals size was slightly higher in SG2 glass-ceramic than SG1 and SG3 materials). Other characterization techniques (EDX, TEM...) could be used in future experiments in order to be more precise on the structure of all the formed crystals and to accurately evaluate the amount of residual glass.

Some crystals of hexacelsian $BaAl_2Si_2O_8$ phase could be present (traces) in SG1, SG3 and SS1 glasses due to the fact that some major diffraction peaks of this pattern (22,48°, 30,08°, 33,82° and 40,99° from the PDF 01-088-1048) match with obtained diffraction data. However, any fine dark needles representing these crystals were observed on the micrographs (Fig. 6c). The presence of large pores is

Table 2
Characteristic temperatures of as-formed glasses using DSC and HSM.

Sample	T_g	T_X	T_C	T_S	T_{HB}	T_F
SG1	596	706	793	705	948	1012
SG2	582	697	751	900	930	964
SG3	577	719	752	902	962	1004
SS1	600	716	763	786	901	971

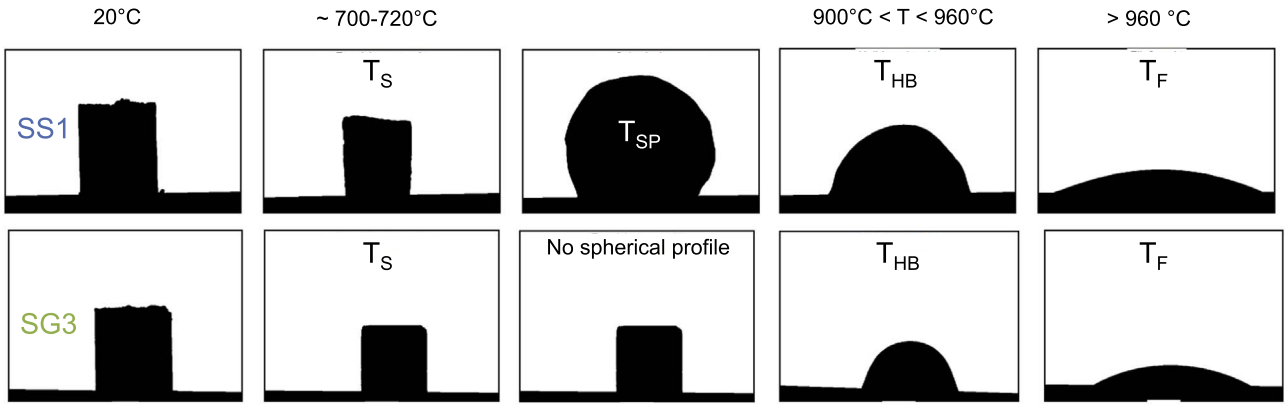

Fig. 3. Rheological behavior of SS1 and SG3 glass pellets versus temperature with HSM from ambient temperature to flow temperature TF (no spherical shape in case of sol-gel glasses).

undesired in sealing process for SOFC applications due to the fact that it will degrade the electrical performances of the cells. So, supplementary investigations (ageing treatment and structural observations) were not realized on SS1 glass. For the glasses made by sol-gel route, the diffraction patterns obtained after an ageing treatment of 100 h at 800 °C were almost the same (Fig. 7), which proved the glass-ceramics obtained after the sealing treatment were already stable versus high temperature treatments.

The measured CTE of the as-formed glasses were in the range of $10{\cdot}10^{-6}\ K^{-1}$ – $13{\cdot}10^{-6}\ K^{-1}$ (Fig. 8). CTE of sol-gel glasses were very close from $12.3{\cdot}10^{-6}\ K^{-1}$ to $12.9{\cdot}10^{-6}\ K^{-1}$ while CTE of SS1 glass was lower. After a heat treatment at 850 °C during 2 h (simulation of a sealing procedure), CTE of glass-ceramics were in the range $10.9–11.9{\cdot}10^{-6}\ K^{-1}$. However, the error on the CTE measurement of SS1 glass-ceramic was bigger than $\pm 1.10^{-6}\ K^{-1}$ (> 10%) due to the big pores present in the samples.

Using an ageing treatment at 800 °C during 100 h on the same samples after the previous treatment, the CTE of the glasses synthesized by the sol-gel route stabilize around $10.9–11.2{\cdot}10^{-6}\ K^{-1}$.

4. Discussion

Considering SOFC applications at 700–800 °C, the barium silicate glasses often have T_g between 575 °C and 685 °C [9,11,12,16]. In this study, the low measured T_g of the glasses are in the range 580–600 °C. In order to obtain a rigid seal with high mechanical properties, it is necessary to have strong devitrification in glasses and to avoid glass flow during the sealing operation. So, sealing temperature must be in the range [T_C - T_{HB}] to satisfy these criterions. A pressure could be applied to facilitate joining procedure in case of a high contact angle. Considering these essential facts and the results issued from Table 2, it appeared possible to seal an SOFC with the proposed glasses at 800–900 °C. The use of a heat treatment at 850 °C was perfectly adapted to simulate sealing conditions although only 800 °C could be use in future investigations in order to lower the thermomechanical constraints on other SOFC components. Concerning the ageing treatment, last promising results had already been obtained using SG1 or SG2 glasses at 700–800 °C in different atmospheres indicating that these glasses could be used at an intermediate temperature of 700 °C [24–26]. The ageing treatment at 800 °C under air atmosphere chosen in this study was adequate to evaluate the synthesized glasses under more severe operating conditions.

Large pores were formed at temperatures over 760 °C in SS1 glass, which allow to reach a spherical shape at ~850 °C (Fig. 3). Furthermore, after 2 h at 850 °C, SS1 glass-ceramics remained very porous due to the fact that crystals maintained mechanical properties of the formed porosity (Fig. 4). Although SS1 glass appeared homogeneous after glass processing, $BaCO_3$ could not have been fully decomposed because this compound generally decomposes into BaO and CO_2 at temperatures close to 1300–1400 °C. Furthermore, due to the reactivity of $BaCO_3$ with SiO_2 at low temperature, this compound could be decomposed at lower temperatures, which proves that the formed glass using solid-state route was not so homogeneous. So, the pores correspond to CO_2 bubbles and it is necessary to use a higher glass processing temperature to ensure that $BaCO_3$ is fully decomposed. Carbonates generally allow to obtain homogeneous glass at lower temperature and the use of another BaO precursor would not have similar effect or homogeneous glass could be obtained only at higher temperature.

In the case of sol-gel glasses, sintering and crystallization steps were considered as independent phenomena as no large pores were observed (Figs. 3 and 4). Considering that T_X-T_g difference of SG3 glass is around 30 °C higher than for the other glasses, this glass is more stable against crystallization process above T_g, which proved the adequate homogeneity obtained in this glass processed at the lower temperature (1100 °C). Although no calculations had been done on the crystallization rates, it appeared that these rates were higher in SG2 and SG3 glasses than in SG1 material as the measured T_S were higher (Table 2). These glasses have been ground at a smaller grain size than SG1 material before the thermal analyses. So, a higher specific area was obtained and the glass reactivity over crystallization processes at high temperature was increased. This result demonstrates that the grain size

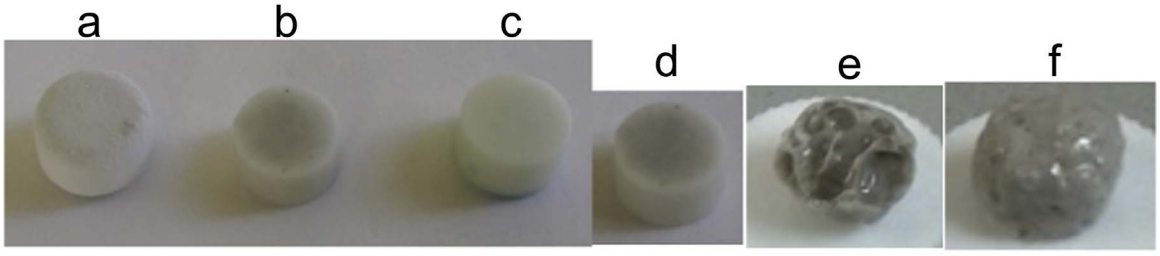

Fig. 4. Photographs of pellets made with glass powders a) without thermal treatment (Ø 6 mm), and b) to f) after 2 h at 850 °C with respectively from the left to the right SG1, SG3, SG2, SS1 (bottom) and SS1 (top) pellets.

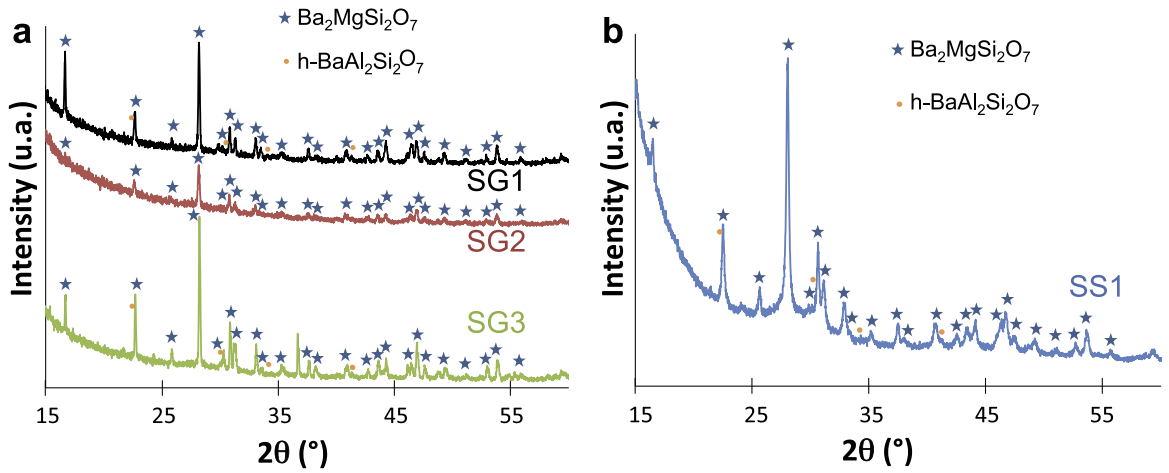

Fig. 5. XRD pattern (obtained at room temperature) of a) SG1, SG2 and SG3 glass-ceramics formed after a heat treatment at 850 °C- 2 h, b) SS1 formed after a heat treatment at 850 °C- 2 h.

of the glass powder obtained before the sealing operation (for all synthesis processes to make the glass) is very determining to select the right sealing temperature/process and will greatly participate to the success of the operation and to the long-term stability of the seal at high temperature.

Concerning the major identified crystalline phase, the CTE of monoclinic $Ba_2MgSi_2O_7$ is around $8{\cdot}10^{-6}$ K^{-1} [10], which could explain the slight decrease of the CTE of sol-gel glass-ceramics during the first hours of devitrification at high temperature. However, barium calcium silicates and barium silicates with high CTE ($9–14{\cdot}10^{-6}$ K^{-1}) generally crystallize in BCAS glass [32]. The presence of these minor phases allowed to maintain the CTE of glass-ceramics at higher values close to $11–12{\cdot}10^{-6}$ K^{-1} (Fig. 8). According to literature, hexacelsian $BaAl_2Si_2O_8$ was present in several barium boron aluminosilicate glasses after thermal treatments of few hours at 800–900 °C and could transform over time at high temperature (100–200 h) into monocelsian phase, which could degrade their thermomechanical properties [10,32]. Presence of hexacelsian phase was suspected but microscopic observations did not prove it. Furthermore, no monocelsian phase $BaAl_2Si_2O_8$ was identified in the glass-ceramics after sealing and ageing operations. These phases could be absent due to the weak Al_2O_3 content in as-formed glasses and the formation of hexacelsian $BaAl_2Si_2O_8$ did not depend on the synthesis process in the present case.

The similar CTE values obtained after sealing and ageing treatments were expected due to:

- Similar chemical composition used in the sol-gel process,
- Similar crystalline phases identified in the materials with nearly similar crystals size,
- The amount of crystalline part, which appeared to be very close in the formed glass-ceramics as it had been observed on micrographs (Fig. 6).

CTE of materials synthesized using a sol-gel route is slightly

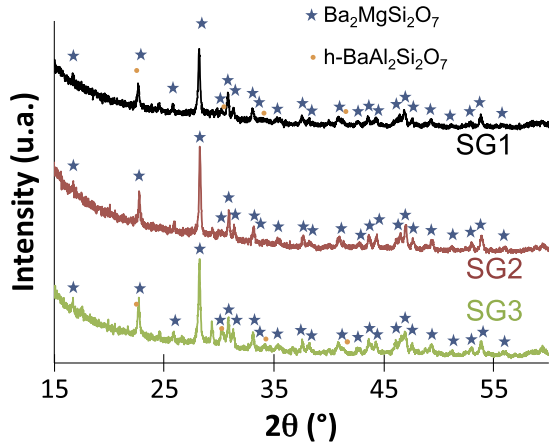

Fig. 7. XRD pattern (obtained at room temperature) of SG1, SG2 and SG3 glass-ceramics formed after a heat treatment at 800 °C-10 h.

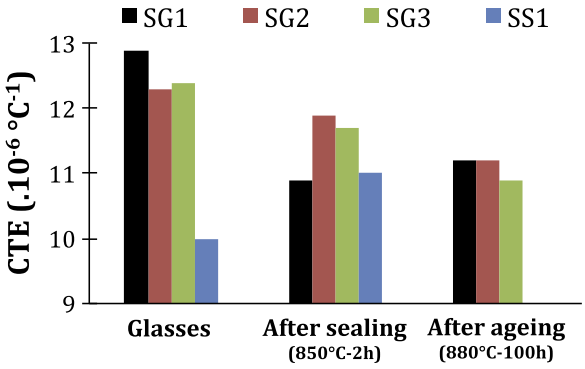

Fig. 8. Results of the CTE measurements from 200 to 550 °C after glass processing, sealing and ageing treatments.

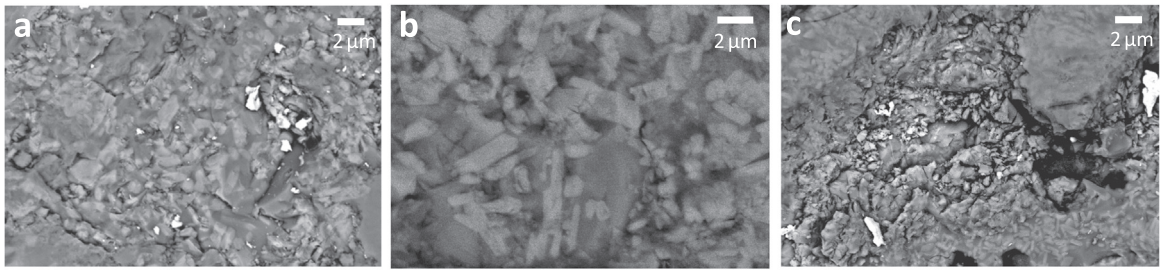

Fig. 6. Backscattered electron micrographs of glass-ceramics a) SG1, b) SG2, c) SG3 after 2 h at 850 °C.

increased or reduced after the ageing treatment of 100 h at 800 °C, which proved their good thermal stability. Therefore, stable thermo-mechanical and structural properties were well correlated, which argue positively on a long-term stability of the three sol-gel glasses. CTE of these glasses remained between CTE of common steel interconnector (notably K41x and CROFER22APU) and CTE of electrolyte (8-YSZ) after the heat treatments.

Considering all the results, it appeared that the processing temperature can be reduced at 1100 °C during 1 h for glasses synthesized by the sol-gel route (SG3), taking into account that sintering musts occur before crystallization step during the sealing process with a slow heating rate (close to 1–2 K min^{-1}). As the grain size will influence the crystallization rate, the use of bigger glass grains with a median size in the range 10–20 μm will allow to optimize the sealing procedure. Concerning SS1 glass synthesized by solid state route, the use of 1300 °C as final processing temperature is not adequate. It would be better to use directly BaO instead of $BaCO_3$ in the initial mixture and to reach the melting around 1500–1600 °C. Observing the obtained first results, this glass could have similar properties compared to sol-gel glasses but it must be confirmed by further investigations because metastable hexacelsian phase could be promoted with a different heating procedure. This process will need much more energy than the optimized sol-gel one at 1100 °C due to the higher temperature involved.

5. Conclusions

Four amorphous barium boron aluminosilicate glasses with the same chemical composition were developed using different routes. Using similar conditions as in a sealing operation, the glass SS1 (solid-state route) was not adapted for an SOFC application due to the formation of large pores (CO_2 emissions during the decomposition of $BaCO_3$ compound). So, the use of other precursor of BaO is necessary in the initial mixture in the solid-state route but it will increase the energy input involved in the final process in order to reach higher temperature. Taking into account the crystallization phenomenon into the glasses SG1, SG2 and SG3 during a sealing operation, it appeared that it is necessary to have a glass powder with grain sizes in the range 10–20 μm. A lower grain size will increase the glass stability over crystallization but it will also increase the crystallization rate when the temperature is in the range [T_X-T_C] (SG2 and SG3 glasses). Monoclinic $Ba_2MgSi_2O_7$ is the main crystalline phase formed during devitrification. Crystalline phases and microstructure of the formed glass-ceramics remained nearly similar after sealing procedure and after ageing treatment in air atmosphere, which proved that these materials are promising for a long-term operation at high temperature. Furthermore, the CTE of SG1, SG2 and SG3 glasses remained close to the CTEs of the steel interconnector and of the electrolyte, which indicates that these sealants were promising candidates for SOFC applications at 700–800 °C (maybe also at 650 °C). Finally, the use of a lower glass processing temperature at 1100 °C (SG3) allowed to obtain similar homogeneity in glasses and glass-ceramics after devitrification at high temperature. So, the glass processing temperature for future investigations will be fixed at 1100 °C, which is 400–500 °C below the glass processing for almost all glass seals used for this application.

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