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Sol–gel synthesis and characterization of barium (magnesium) aluminosilicate glass sealants for solid oxide fuel cells

J. Puig [a,*], F. Ansart [a], P. Lenormand [a], L. Antoine [b], J. Dailly [c]

[a] *CIRIMAT, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France*
[b] *ADEME, 20 Avenue du Grésillé, BP90406, 49004 Angers Cedex 01, France*
[c] *EIFER/EDF, Universität Karlsruhe, Emmy Noether Strasse 11, 76131 Karlsruhe, Germany*

ABSTRACT

Solid oxide fuel cells (SOFC) correspond to efficient energy conversion systems coupled with low emissions of pollutants. In the aim to fabricate high temperature planar SOFC, glass and glass-ceramic sealants are developed to associate several criteria and properties : high thermal expansion (11.0 to $12.0 \cdot 10^{-6}\,K^{-1}$), high electrical resistance$>2\,k\Omega/cm^2$, good thermochemical compatibility with the other active materials of the fuel cell, and stability under H_2 and H_2O atmospheres at an operation temperature of 800 °C for a long time. According to these requirements, new BAS ($BaO-Al_2O_3-SiO_2$) and BMAS ($BaO-MgO-Al_2O_3-SiO_2$) glass-ceramic sealants have been developed by sol–gel route which is a non-conventional process for such applications. By this soft chemistry process, we anticipate a decrease in the glasses processing temperature due to a better homogeneity between cationic precursors in the mixture and a more important reactivity of materials. Experimental results in terms of thermomechanical properties, thermal expansion coefficient, crystalline phase content, and microstructure were discussed. In particular, the influence of the %BaO on the thermomechanical properties of glass-ceramics was described. Changes in properties of glass-ceramics were closely related to the microstructure. The influence of MgO on glass processing temperatures, on the structure and on the microstructure is evaluated in order to confirm that these glass-ceramics are promising candidates to SOFC applications. So, after performing a systematic investigation to the various systems, the properties of suitable glass were proposed.

1. Introduction

Nowadays, main energetic resources come from fossil fuels which throw a lot of pollutants like SO_2, NO_x, CH_4, chlorofluorocarbon compounds and CO_2 in atmosphere. All the countries in the world are trying to reduce the use of fossil fuel with the signature of draft agreements (Kyoto 1997, Copenhagen 2010). As a consequence, research and development on new and green energetic resources are increasing more and more.

SOFC are great candidates to solve this problem because of their high efficiency energy conversion systems (70–80% with cogeneration) and their low emissions of pollutants [1]. SOFC working is to convert directly chemical energy of a redox reaction to electrical energy. The reaction heat can be reused to supply the cell working temperature (600–800 °C) and, for example, to heat a water circuit.

The reactants are the air and Hydrogen (or in some cases, CH_4, or a natural gas) and the unique reaction product is water [1,2]. These cells have a great potential for power generation either in stationary or in mobile applications. Recent works on this field attempt to optimize the constituents and to reduce the cells cost in order to identify SOFC as a sustainable technology [3].

For the past 10 years, the laboratory is working on the planar SOFC development (materials synthesis and coatings processing) using the sol–gel route which is a low cost process. Recently, different cells mechanically supported by the anode or by a porous metal have been tested [4]. In order to make a Serial Repeat Unit (SRU), the new focus is the development of glass-sealant to separate the cathodic and anodic compartments [5]. Indeed, it is necessary to ensure the cells gas tightness to increase the SRU durability. Moreover, the sealant must be chemically compatible with the other cell components. Finally, the sealing material must resist to thermal stresses due to heating and cooling cycles of a stack.

Glass-ceramic sealants are great candidates for this application because of their good mechanical properties and the possibility to use a wide range of chemical compositions to control some physico-chemical properties such as viscosity, coefficient of thermal expansion (CTE) and glass transition temperature.

* Corresponding author.
  E-mail address: puig@chimie.ups-tlse.fr (J. Puig).

Among the most promising materials, glass-ceramic sealants have been extensively studied [5]. Barium silicates and barium magnesium silicates (made by "glass classical process") have suitable properties to be used as glass-sealant. Several compositions have been studied in the literature. In the last decade, several innovative glasses have been also developed to identify the respective contribution and influence of each addition element. For instance, the glasses with the presence of a small quantity of Mg are well known to present a suitable thermal expansion coefficient for their use in SOFC ($8-11 \times 10^{-6} K^{-1}$) [6]. Barium silicates crystallize in all the glasses, while barium magnesium silicates can be promoted or inhibited as a function of additive elements. The addition of B_2O_3 produces an expected decrease of viscosity and delay in the crystallisation which leads to a greater wettability of the glasses on the steel and then, to a better bonding, which inhibit the formation of $BaCrO_4$. These compositions result in partially crystallized materials with a relatively large glassy phase volume [6].

In the works of Ghosh et al. [7], the effect of BaO addition is reported on thermal, crystallization, electrical and mechanical behavior of the magnesium lanthanum alumino borosilicate glass-ceramics. The glass forming region has been found to be quite narrow with respect to BaO content. Casting and annealing of completely transparent and amorphous glasses within this system has been possible only at an optimum BaO content of 25 mol% without any La_2O_3 and Al_2O_3. On further optimization of the developed glasses in terms of different borosilicate ratios, one of the developed compositions having MgO and BaO content of 22 and 25 mol% respectively, with a glass former ratio of 3 (SiO_2:B_2O_3) has been found to be quite promising in terms of its mechanical property, excellent joining, minimum chemical interaction and lowest leak-rate with the metallic interconnect such as Crofer22APU, and thus fulfills the major requirements for SOFC sealing application [7].

By other authors, glasses from the system MO (M = Mg, Ca)–Al_2O_3–BaO–SiO_2–B_2O_3 were developed and evaluated as SOFC sealants and show a good thermal expansion match with metallic interconnect materials, especially with Crofer22H between the glass transition temperature Tg and room temperature. The developed glass-ceramic composites have a high remaining residual glass phase of 60 wt.% compared to 40 wt.% crystals, which primarily consist of Ba4Si6O16-silicates [8].

So taking into account all these previous studies and formulations, the objective in this paper has been to propose a new non-conventional process coming from soft chemistry techniques. In fact, in the SOFC applications field, two main issues have to be solved: 1) the reduction of costs and the sol–gel route is well known to be a low cost technique and 2) to reply to a very important number of criteria and in particular the decrease of the shaping temperature of glasses [9]. By this process, the reduction of the glass processing temperature is possible due to a better homogeneity in the cationic salts mixture compared to solid state routes (macroscopic mixture of simple oxides).

After having demonstrated that it would be possible to reach this aim, we will discuss the results in terms of thermomechanical properties, thermal expansion coefficient, crystalline phase content and microstructure. The influence of compounds such as BaO content on the thermomechanical properties of glass-ceramics will also be described. On the same way, the influence of MgO on glass processing temperatures, on the structure and on the microstructure will be evaluated in the framework of SOFC applications. Many studies showed that the use of gel mixture could decrease the temperature formation of glasses of 100–200 °C below those required using conventional batch material [10] and authors have shown that the synthesis by sol–gel route of barium aluminosilicates was possible [10–13].

So, in this paper, the first step has been to give details on the oxide powder synthesis by sol–gel route we have used. After the glass processing, first characterizations showed the influence of %BaO on the thermomechanical properties of glass-ceramics. The role of MgO on the structure and microstructure of these glass-ceramics is evaluated too.

2. Experimental procedure

2.1. Oxide powder synthesis by sol–gel route

The multi-component silicate gels were prepared using the alkoxide route. Different parameters such as pH, H_2O/TEOS ratio (W) and CH_3COOH/TEOS ratio (R) were monitored during the synthesis.

The precursor material used to prepare the oxide batches were tetraethylorthosilicate (TEOS), aluminum tri-sec-butoxide (ASB), barium acetate and magnesium acetate. All reactions were performed under constant stirring conditions in polypropylene containers.

Fig. 1 presents the different steps of the chemical preparation procedure used to synthesize final oxide powders. The two alkoxides had two different hydrolysis rates. The TEOS reacted more slowly with water than the ASB. As a consequence, a partial hydrolysis of the TEOS was necessary to obtain homogeneous mixtures. HCl was the catalyst of the hydrolysis. After the second step (slow addition of aluminum alkoxide diluted in isopropanol), ASB and TEOS reacted during 12 to 14 h to ensure complete reaction. Then, acetates (pre-diluted in water and acetic acid) were added. The barium acetate was not very soluble, so W ratio was high (around 20 to 45) and the gelation occurred rapidly (within a few hours). Neither precipitation nor phase separation occurred during the sol–gel transition. Finally, gels were dried in a furnace at 80 °C during one day and then calcined at 850 °C during 4 h.

Different chemical compositions have been investigated in order to understand the role of barium oxide and magnesium oxide in sol–gel glasses (Table 1).

The calcination temperature was kept constant at 850 °C according to DTA and XRD characterizations yet realized (750 °C during 12 h reduced to 4 h at 850 °C) [10]. Indeed, this high temperature is necessary to eliminate barium carbonates (formed during the sol–gel transition and during the heat treatment).

2.2. Glass-ceramic processing

As the glass processing temperature of the future sol–gel glasses was not well known, pellets (diameter 6 mm, thickness 1.5–3.5 mm) of glass oxide powders were prepared and heated from room temperature to 850 °C, 1000 °C, 1150 °C and 1300 °C.

BMAS1 and all BAS glass-ceramics were formed at 1300 °C during 10 min with a heating rate of 100 °C/h from room temperature to 1300 °C. BMAS2 and BMAS3 glasses were formed at only 1150 °C with the same heating rate (Fig. 2). So the magnesium compound seems to have a key role in the decrease of the glass formation temperature compared to the barium.

2.3. Characterization of glass-ceramics

Measurements of CTE (coefficient of thermal expansion) as a function of temperature were conducted on 6 mm (diameter) × 1.5–3.5 mm (thickness) pellets of bulk glass using a dilatometer (sensor SETSYS Evolution TMA). Coefficients of thermal expansion were calculated between 150 °C and 600 °C under air atmosphere and three pellets of each chemical composition have been characterized.

The XRD equipment used to characterize the structure of glass-ceramic samples is a BRUKER AXS D4 Endeavor operating in Bragg–Brentano mode (θ–2θ). All scans were performed between 10° and 100°.

A SEM equipment JEOL JSM-6510LV apparatus was used to determine the microstructure of the glass-ceramics samples (i.e. size and morphology of the crystal, porosity).
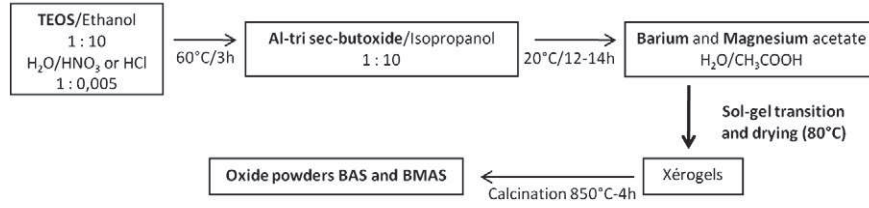
Fig. 1. The chemical preparation procedure.

3. Results

3.1. Structure and microstructure of glass-ceramics

3.1.1. BAS glass-ceramics

All the glass oxide powders were analyzed by XRD technique before the glass-ceramic processing. The BAS powders included a major amorphous phase and only two crystalline phases were identified for all chemical composition from BAS1 ($55BaO–5Al_2O_3–SiO_2$ bal. mol%) to BAS 5 ($15BaO–5Al_2O_3–SiO_2$ bal. mol%): a major phase Ba_2SiO_4 and a minor phase $Ba_6Si_{10}O_{26}$.

After the glass-ceramic processing at 1300 °C, various crystalline phases were also identified. All the glass-ceramics included a high amount of residual glass phase and all the identified crystalline phases belonged to barium silicates family (Fig. 3). SEM micrographs (Fig. 4) showed needle-like crystals dispersed into an amorphous matrix of the BAS glass-ceramics. EDS analysis confirmed that the elongated crystals (10 to 50 μm long with a thickness of 1 to 3 μm) consisted of barium silicates and that the gray smooth areas were the residual amorphous glass phases identified as barium aluminosilicate. The darker areas were not clearly identified. Nevertheless, these areas could be assimilated at Al_2O_3 as Bansal and al. described [14]. No hexacelsian phase was detected after the glass processing. The crystallization appeared in surface as well as in the bulk of these glasses. Consequently, such BAS glass-ceramics were homogeneous.

3.1.2. BMAS glass-ceramics

One of the aims of this study was to determine the role of MgO in a barium aluminosilicate glass ceramic. As a consequence, three different chemical compositions with MgO were selected (Table 1):

– BMAS1 with a weak content in MgO and a ratio BaO/MgO = 3.5
– BMAS2 which is an intermediary chemical composition with a ratio BaO/MgO = 2.5
– BMAS3 with a high content in MgO and a ratio BaO/MgO = 0.3

Similar to the process used for the BAS, all the BMAS glass oxide powders were analyzed by XRD technique before the glass-ceramic processing. The BMAS powders included a major amorphous phase and different crystalline phases were identified: $BaMg_2Si_2O_7$ in BMAS1 powder, many barium silicates in BMAS2 powder and Ba_2SiO_4 in BMAS3 powder.

After the glass-ceramic processing at 1300 °C for BMAS1 and 1150 °C for BMAS2 and BMAS3, different crystalline phases were identified (Fig. 5):

– $BaSi_2O_5$ in BMAS2 and $BaSiO_3$ in BMAS3.
– 2 new phases appeared in BMAS1: Mg_2SiO_4 and $MgSiO_3$. The presence of any barium silicate was not detected.

Diffraction pattern peaks were weak indicating that the major phase of the analyzed sample was constituted by a residual amorphous glass (like in BAS glass-ceramics). Fig. 6a shows the presence of barium silicates crystals in an amorphous matrix. The shape of the crystal is different than in the BAS glass-ceramics case. Indeed, these crystals were parallelepipeds contrary to the needle shaped crystals previously obtained. Moreover, the BMAS glass-ceramics samples were very porous and these crystals were not observed in BMAS3 (Fig. 6b).

3.2. Thermomechanical analysis of glass-ceramics

The CTE (Coefficient of Thermal Expansion) of glass-ceramic sealants is one of the most important parameters in SOFC applications because it must match the CTEs of other cell components. The CTE of an YSZ electrolyte is around $10 \cdot 10^{-6} K^{-1}$ to $11 \cdot 10^{-6} K^{-1}$ while this coefficient is around $12 \cdot 10^{-6} K^{-1}$ to $13 \cdot 10^{-6} K^{-1}$ for a metallic interconnector. As a consequence, the CTE of glass sealants must be between these two values in order to avoid new stresses in SOFC components during the heating and cooling cycles.

In that particular case, the steel we have chosen is a low cost steel K41X (Arcelor Mittal) with around a content of 17% Cr.

CTE of YSZ ($92\%ZrO_2–8\%Y_2O_3$) was measured on a pellet of commercial Tosoh powder compacted (400 MPa during a minute) and preheated to 1550 °C.

The CTE of BAS glass-ceramics synthesized by sol–gel process depended on the %BaO of these glasses. Actually, experiments (Fig. 7) showed that CTE of BAS glass-ceramics increases while the %BaO was increasing (except for CTE of BAS4 that is higher than CTE of BAS3).

The glass-ceramics with a BaO content around 25% to 45% (%Mol.) seemed to be the most promising material to seal SOFCs. However, BAS samples had porosity around 10 to 20%$_{vol}$.

The BMAS glass-ceramics were so porous that no CTE measurements can be performed because mechanical integrity of these glasses was not insured. Besides, works to reduce the porosity level in these glasses are in progress.
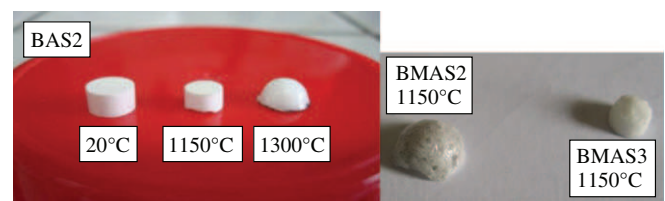
Table 1
Chemical compositions of oxide powders.

Chemical composition (molar %)	BaO	MgO	Al_2O_3	SiO_2	W	R
BAS 1	55	0	5	40	35	5.5
BAS 2	45	0	5	50	25	4.7
BAS 3	35	0	5	60	20	4.7
BAS 4	25	0	5	70	20	3.8
BAS 5	15	0	5	80	20	3.8
BMAS1	10	35	5	50	30	2.5
BMAS2	25	10	5	60	30	2.5
BMAS3	35	10	5	50	45	2.5

Fig. 2. Photographs of glass-ceramics.
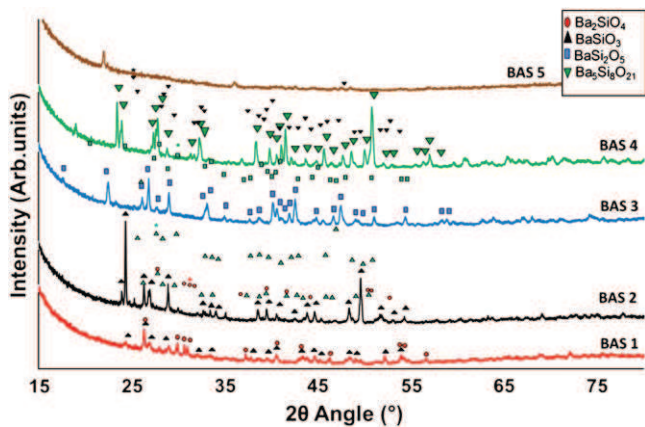
Fig. 3. XRD pattern of BAS glass-ceramics.

Fig. 5. XRD pattern of BMAS glass-ceramics.

4. Discusssion

Although the crystallization phenomenon was not clearly identified when observing the XRD of BAS glass-ceramics, it occurred even with 15%BaO (Fig. 4) and these materials were homogeneous and not very porous. On the contrary, the microstructure of BMAS samples could not be well determined because of its high porosity and it appeared that it is difficult to conclude on the crystallization homogeneity of such compounds by SEM observations.

In the literature, barium silicates crystals had been known to have great CTE. For example, $BaSiO_3$ has a CTE of $12.5 \cdot 10^{-6} K^{-1}$ [14]. Taking into account that BAS4 glass-ceramic is mainly composed of $BaSiO_3$ crystals (Fig. 3), it is obvious that the increase of the CTE is caused by the formation of these crystals (CTE of BAS4 is around $12.3 \cdot 10^{-6} K^{-1}$).

If we investigate the influence of the ratio MgO/BaO, it is important to underline that for BMAS glass-ceramics, crystallized phase observed in BMAS2 corresponds to the same compound ($BaSi_2O_5$) as the one identified for BAS3. The same result has been proved for respectively BMAS3 and BAS2 glass-ceramics (with the phase $BaSiO_3$). So, we can conclude that the balances [35% BaO–25% BaO, 10% MgO] and [45% BaO–35% BaO, 10% MgO] were similar in terms of crystallographic behavior. As a consequence, it seemed that MgO promotes barium silicates crystallizations in the same way as BaO (substitution of BaO) during the glass processing. On the other side, if the ratio of MgO increases, keeping constant the global content MgO + BaO, the conclusion is quite different. So, comparing BMAS1 (10% BaO–35% MgO) with BMAS3 (35% BaO–10% MgO), the equilibrium MgO/BaO is not equivalent since no barium silicate was detected in the case of BMAS1. Consequently, when the BaO content is very low compared to the MgO content, MgO does not promote the crystallization of barium silicates during the glass processing.
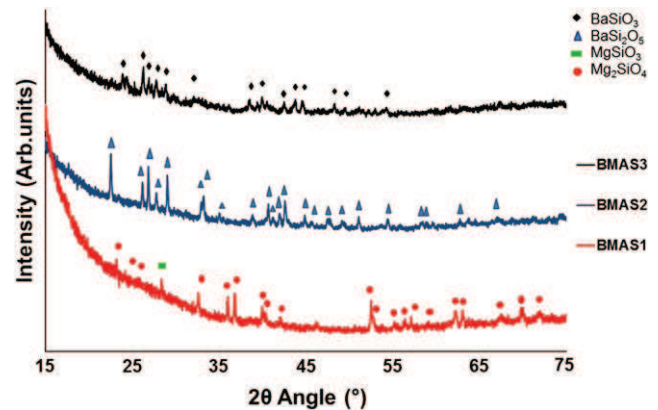
Finally, considering that microstructure is bonded to CTE in glass-ceramics and observing XRD pattern of BMAS, we can evaluate the future values of CTE [14,15]:

- BMAS2 and BMAS3: CTE in the range $10.5 \cdot 10^{-6} K^{-1}$ to $12.5 \cdot 10^{-6} K^{-1}$.
- BMAS1: CTE in the range $9 \cdot 10^{-6} K^{-1}$ to $10 \cdot 10^{-6} K^{-1}$ (CTE (Mg_2SiO_4) = $9.4 \cdot 10^{-6} K^{-1}$).

5. Conclusion

A new chemical preparation procedure using the sol–gel route to develop glass-ceramics sealants for planar SOFC has been investigated. Glass forming temperatures (respectively 1300 °C for all the BAS and BMAS1 and 1150 °C for BMAS2 and BMAS3) are clearly lower than in a conventional solid state processes (oxide batch in the range 1500 °C to 1600 °C). Besides, the presence of MgO with a high BaO/MgO ratio tends to diminish these temperatures (BMAS2 and BMAS3).

Coefficients of thermal expansion, structure and microstructure of glass-ceramics have been studied. From a structural point of view, BAS and BMAS glass-ceramics included a major amorphous phase and various crystalline phases. For the BAS compounds, the tendency, corresponding to the fact that these crystalline phases had a key role on the increase of CTEs, was underlined. This aspect will be pointed out in future work when glass-ceramics porosity will be reduced to improve accuracy of the CTEs values. BMAS glass-ceramics were too porous to characterize the microstructure precisely. However, MgO exhibited a key role as a BaO substitute and could promote the crystallization of barium silicates in a medium range which had been previously described.
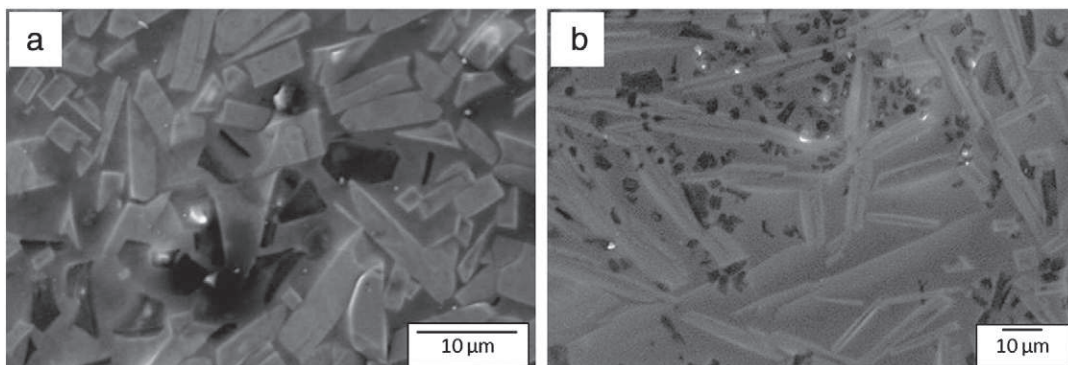

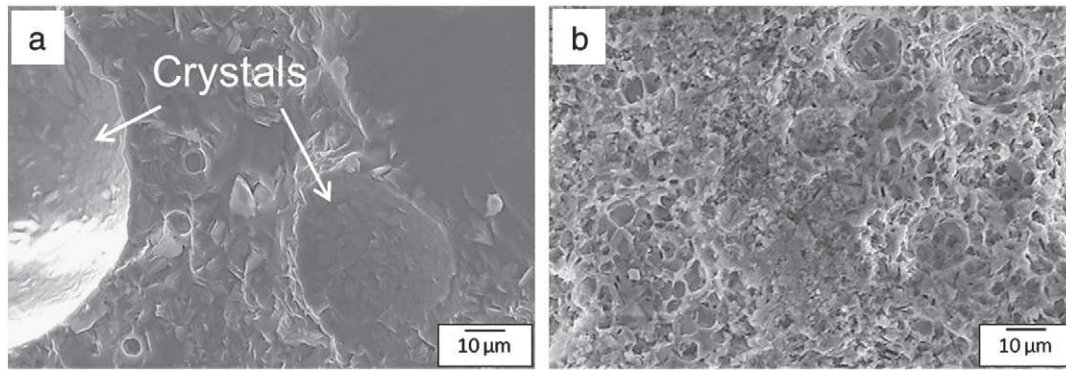Fig. 4. SEM micrographs of BAS2 surface and BAS5 bulk.

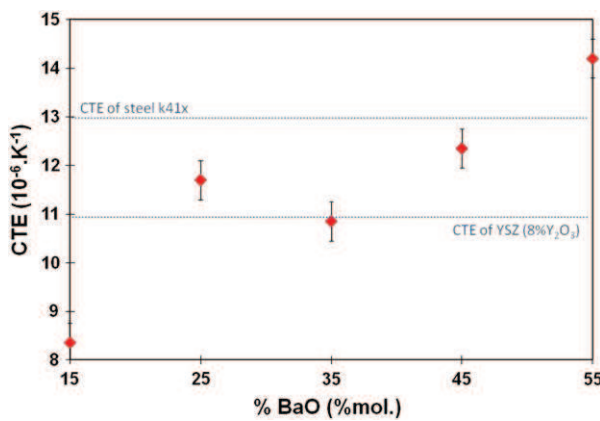**Fig. 6.** SEM micrographs of BMAS2 bulk and BMAS3 bulk.

Fig. 7. CTE measurements of BAS glass-ceramics depending on the BaO content.

Based only on the CTE measurements, it can be concluded that the glass-ceramics BAS2, BAS3 and BAS4 were the most promising glasses for planar SOFC operating at 600 °C–800 °C.

Prospects will focus on the characterization of the glass transition temperature determination and the incorporation of other components like B_2O_3 or CaO in order to investigate and to improve the thermal, mechanical and bonding properties of these glass-ceramics.

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