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Study of the Crystallization in a Glass-Ceramic Seal

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Sealing is a major issue in Solid Oxide Cells (SOC) stacks used for hydrogen production. The specifications that seals must meet are particularly demanding. Glass-ceramics such as materials from the MgO-Al₂O₃-BaO-SiO₂-B₂O₃ system are used. A preliminary treatment allows the initially amorphous material to set up while partially crystallizing. This paper presents the crystallization study of such a material.

The main Ba₅Si₈O₂₁ and BaMg₂Si₂O₇ crystalline phases are identified and the evolution of crystals morphology with the temperature is followed. The Ba_xSi_yO_{x+2y} surface fraction is determined by image analysis as a function of time and temperature. These data allow accessing the equilibrium crystal fraction. It is then possible to optimize the crystallization treatment and to anticipate the microstructural evolution of the glass-ceramic seal operating in the stack.

Introduction

The SOC (Solid Oxide Cell) high temperature electrolysis technology, used for hydrogen production, is based on a successive stack of single electrolysis cells and metallic interconnectors ensuring both the collection of oxygen and hydrogen, and the electronic conduction between the different Single Repeat Units. In such complex systems, ensuring the sealing of this ceramic/metallic multilayer assembly is technically very challenging and the requirements on the sealing material are numerous. It must be compatible with both high temperatures and various atmospheres (H₂, O₂, H₂O), and with the materials to be sealed (compatible thermal expansion coefficients). It must also present specific physical properties (thermal, electrical, mechanical) (1). When combining all the constraints, the list of materials is shrunk to a very small number of potential candidates. Oxide materials, such as glass-ceramics, are the reference materials for such seals (2). A preliminary thermal treatment allows the glass-ceramic used as sealant in SOC to be formed. During this set-up step, and while the seal is operating in the stack, crystallization phenomena take place in the material.

The aim of this work is to study the crystallization of a glass from the MgO-Al₂O₃-BaO-SiO₂-B₂O₃ system. Such systems have been studied as sealants and have shown a good compliance with the seal specifications (2-4). A detailed knowledge of the material

microstructure is necessary in order to optimize the thermal treatment of the glass-ceramic formation and anticipate the possible microstructural evolution of the glass-ceramic seal operating in the stack. The first part of this paper describes the different phases identification and the evolution of crystals morphology as a function of temperature. In the second part, the $Ba_xSi_yO_{x+2y}$ crystalline surface fraction is determined by image analysis as a function of time and temperature.

Experimental

The studied material is from the $MgO-Al_2O_3-BaO-SiO_2-B_2O_3$ system. BaO and B_2O_3 contents are respectively below 35 and 15 mol. %, whereas MgO and Al_2O_3 contents are below 10 mol.%. Such a glass can be obtained by double melting of oxide raw materials with intermediate grinding, in Pt/Rh crucible at $1300^\circ C$, followed by quenching.

Thermal treatments of 1g glassy powder ($d_{50} = 16 \pm 4 \mu m$) are performed in a Pt/Au crucible in the range of $680^\circ C$ to $1000^\circ C$ ($50^\circ C$ steps from $700^\circ C$ with a few intermediate temperatures) and for different durations (2, 24 and 48 hours). Glass samples are heated at $5^\circ C \cdot min^{-1}$ to reach target temperature and are air-cooled at the end of the treatment.

Polished sections of the resulting glass-ceramic samples are analyzed using Scanning Electron Microscopy (SEM SUPRA 55 ZEISS, BRUKER EDS detector) for microstructure and composition determination. X-Rays Diffraction measurements (Panalytical XPERT PRO MPD) are carried out on crushed samples. They are measured using a Cu X-rays source ($Cu K\alpha_1 = 1.5406 \text{ \AA}$), Bragg-Brentano geometry and X'Celerator lineal Detector. The acquisition program lasts 5 hours, on a $10-90^\circ$ angular range with a 0.017° step for usual analysis.

Electron BackScatter Diffraction analysis (SEM SUPRA 55 ZEISS with EBSD e-flash BRUKER camera) was performed on a specific sample.

Results and discussion

This section is dedicated to the glass-ceramic characterization. Phases are first identified, crystal morphology evolution with temperature is then discussed. Then, the $Ba_xSi_yO_{x+2y}$ crystalline surface fraction is quantified by image analysis as a function of time and temperature.

Phases identification

Figure 1 displays a SEM image of a sample heated at $750^\circ C$ for 48 hours. It is characteristic of the obtained glass-ceramic microstructure. Three different crystalline phases are observed: a Ba-rich phase (light grey polyhedral crystals, $< 10 \mu m$), a Mg-rich phase (dark slats) and an Al-rich phase (very small needle-like dark crystals, $< 5 \mu m$), as indicated by the cartography (Figure 2) and EDS analysis.

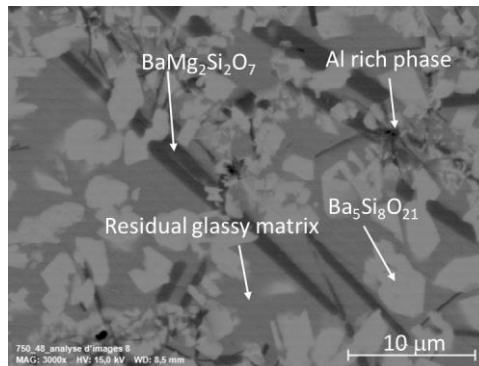


Figure 1 BSE-SEM image of the glass powder sample heated at 750°C for 48 hours.

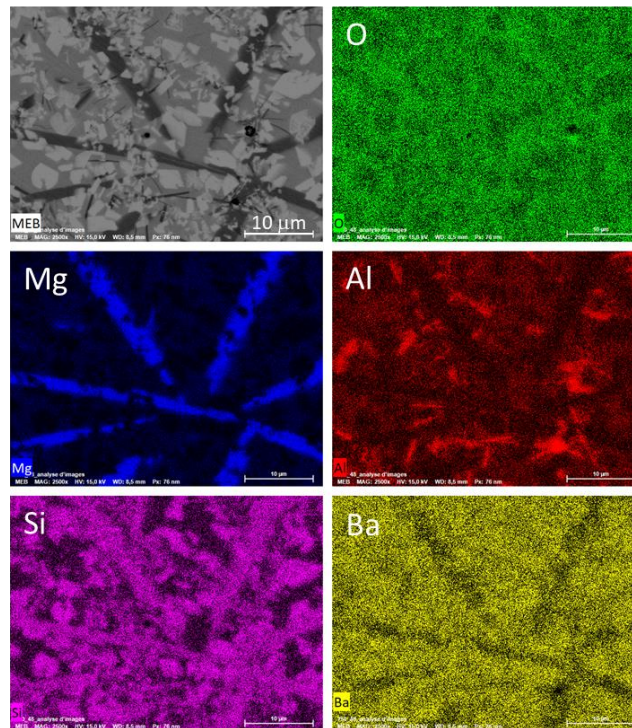


Figure 2 Elemental EDS cartography of the glass powder sample heated at 750°C for 48 hours.

The two main crystalline phases have been further identified by XRD analysis (Figure 3) and correspond to $Ba_5Si_8O_{21}$ (light grey polyhedral crystals) and $BaMg_2Si_2O_7$ (dark slats) which is in agreement with the performed EDS analysis. However, not all peaks on the XRD pattern could be attributed and the Al-rich phase could not be clearly identified. Indeed, those crystals are too small to be analyzed by EDS (smaller than the SEM interaction volume), and in too low content to be detected by XRD measurements. EDS composition profiles confirmed that these crystals are Al and likely Si-rich. Analysis are still in progress.

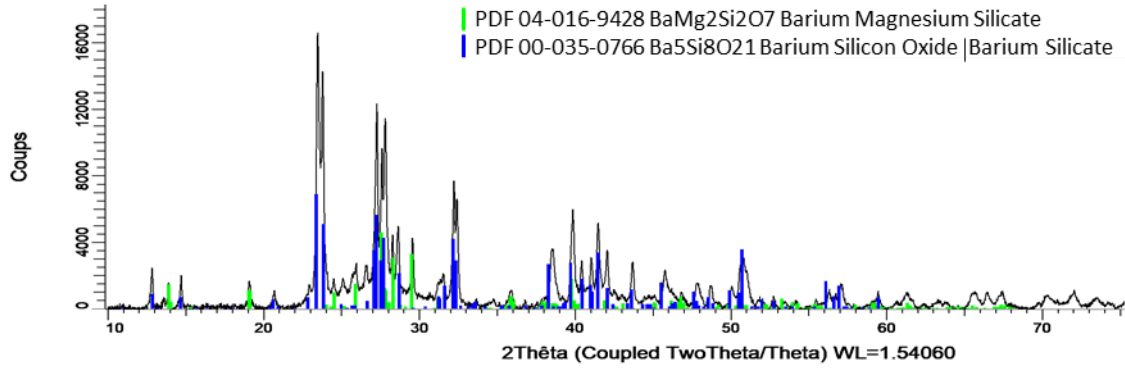


Figure 3 XRD pattern of the sample heated at 750°C for 48 hours (after background subtraction) and Ba₅Si₈O₂₁ and BaMg₂Si₂O₇ phases identification.

Phases evolution with temperature

The 48h thermal treatments at temperatures ranging from 680 to 1000°C (50°C steps from 700°C, with 975°C additional temperature) and the subsequent SEM analysis allow to determine the thermal domains of the crystalline phases forming in this specific system (Table I). The polyhedral Ba₅Si₈O₂₁ crystals are the first to appear, between 680°C and 975°C. Their liquidus temperature is between 975°C and 1000°C. Secondly, the BaMg₂Si₂O₇ slats grow very quickly in length (up to ~ 150 μm) from 700°C to 850°C, and tend to widen with increasing temperature (from ~2 to 10 μm). Their existence domain is a little narrower since their liquidus temperature is between 850 and 900°C. Finally, the Al-rich phase shows the narrowest domain, from ~750°C to ~800°C.

TABLE I. Crystals characteristics with temperature (48h treatment)

Crystals/phase	Ba ₅ Si ₈ O ₂₁	BaMg ₂ Si ₂ O ₇	Al-rich phase
Existence domain	680 to 975°C	700 to ~850-900°C	~ 750 to 800°C
Morphology	Polyhedral 1 to 8 μm	Slats Length up to 150 μm Width from ~2 to 10 μm	Needle-like ~5 μm

Concerning the polyhedral crystals, even if SEM images do not differ, XRD patterns reveal that for low temperatures, there is a shift in the diffraction peaks around $2\theta = 24^\circ$ (Figure 4). Thus, for the sample treated at 680°C, XRD pattern leads to a very similar Ba₂Si₃O₈ crystalline phase. Ba_xSi_yO_{x+2y} crystals are likely changing stoichiometry with the temperature rising in the 680-750°C range. Above 750°C, the stoichiometry is kept constant. When referring to temperatures in the 680-950°C range, we will further name the phase Ba_xSi_yO_{x+2y} in this paper.

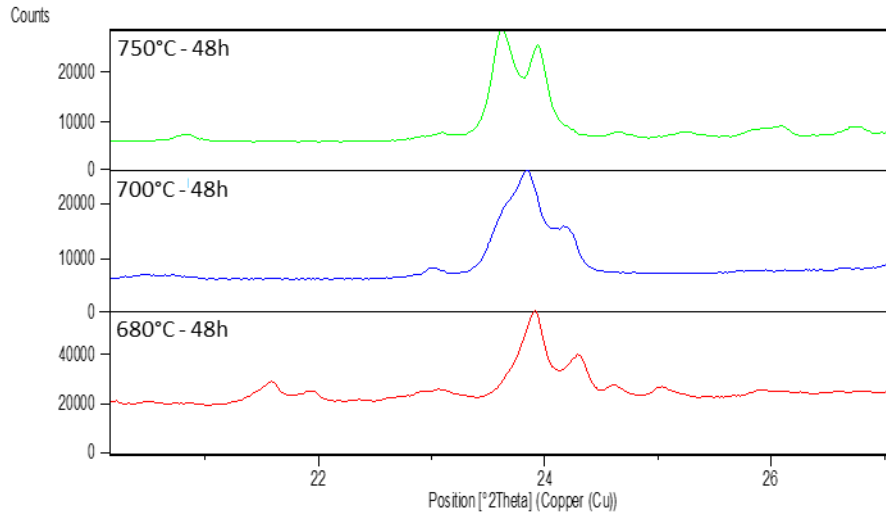


Figure 4 XRD patterns of 680, 700 and 750°C samples (48h treatment), in between 20 and 27° (2theta).

Ba_xSi_yO_{x+2y} crystalline surface fraction

Further quantitative analysis have been performed on the samples in order to determine Ba_xSi_yO_{x+2y} crystals surface fraction. This will also be applied to the BaMg₂Si₂O₇ crystals.

Image analysis. SEM images show a good contrast between the Ba₅Si₈O₂₁ crystals and the rest of the sample. However, they always seem to cover the BaMg₂Si₂O₇ slats. In order to verify that the SEM image analysis is appropriate to quantify the surface of these two types of crystals, an EBSD analysis was performed (Figure 5). BaMg₂Si₂O₇ crystals show the same crystallographic orientation all along their length despite the presence of Ba₅Si₈O₂₁ crystals apparently ‘covering’ them.

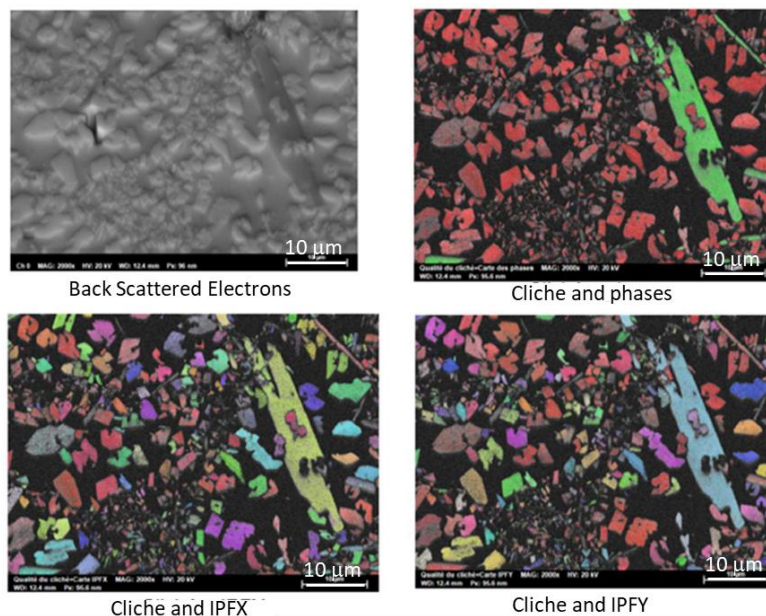


Figure 5 EBSD images of the sample heated at 750°C for 48 hours.

$\text{BaMg}_2\text{Si}_2\text{O}_7$ crystals' growth is not affected by those polyhedral crystals and in fact they are growing around them, as poikilitic crystals (5). This is in agreement with the $\text{BaMg}_2\text{Si}_2\text{O}_7$ crystals rapid growth observed and attested by their slat-shape.

The surface crystallization percentage is determined by processing SEM images (ImageJ software). A x1500 magnification and 6 images (areas free of porosity) allow a good resolution of each crystal and a good representativeness of the sample. The first step consists in binarizing the image, and then converting it to gray levels. A thresholding is then carried out according to the light intensity in order to distinguish the $\text{Ba}_x\text{Si}_y\text{O}_{x+2y}$ crystals from the rest of the sample (Figure 6).

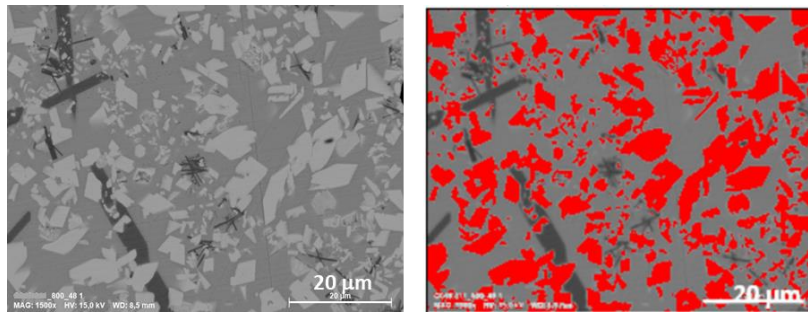


Figure 6 Illustration of the SEM image analysis for the $\text{Ba}_5\text{Si}_8\text{O}_{21}$ crystals (750°C, 48h).

Quantitative results. Figure 7 displays the $\text{Ba}_x\text{Si}_y\text{O}_{x+2y}$ crystalline surface fraction as a function of time for various temperatures. The change in kinetics as a function of temperature is clearly to be seen: whereas, for temperatures less than or equal to 680°C, the equilibrium is not reached after 48h, at 700°C the equilibrium crystalline fraction seems to be reached after 24 h. At 800°C, it seems to be reached after only 2h.

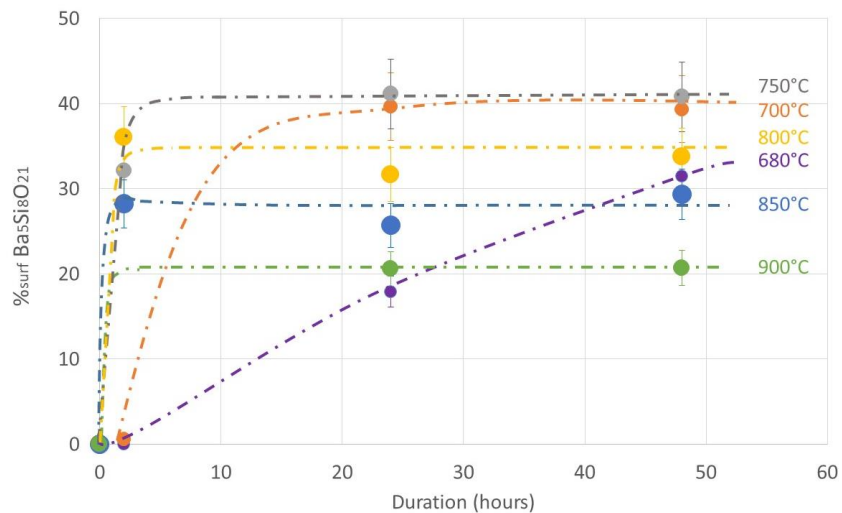


Figure 7 Evolution of the $\text{Ba}_x\text{Si}_y\text{O}_{x+2y}$ crystalline surface fraction as a function of time, for different temperatures – *Dotted lines are traced for the eyes.*

Figure 8 displays the previous data as a function of temperature for different heat treatment durations. This allows to access to the equilibrium $Ba_xSi_yO_{x+2y}$ crystalline fraction (thick dotted line) as a function of temperature. The equilibrium is reached very quickly above 750°C . This also confirms that the liquidus temperature of those crystals in this system is in between 975°C and 1000°C . To complete those data, a Johnson-Mehl-Avrami-Kolmogorov model (JMAK) (6,7) will be applied to this system and the kinetics and Avrami parameters will be determined. This will allow the calculation of the crystallized fraction after isothermal heating at a given temperature and for a given duration. The restriction in this system is that different phases are crystallizing, potentially interacting, and thus changing the equilibrium state. The same approach will also be applied for the other crystallizing phases.

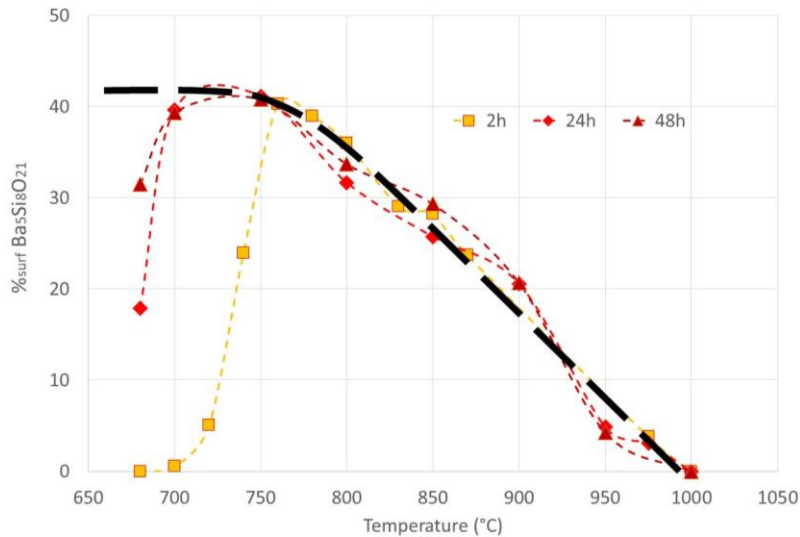


Figure 8 Evolution of the $Ba_xSi_yO_{x+2y}$ crystalline surface fraction as a function of temperature, for different thermal treatment durations – *The thick dotted line is a guide for the eyes.*

Conclusions

A glass-ceramic obtained after thermal treatments of a $MgO-Al_2O_3-BaO-SiO_2-B_2O_3$ glass and designed as sealant in SOC stacks, has been characterized. Thermal treatments were performed in the range of 680 to 1000°C . The glass-ceramic consists mainly of a barium silicate crystalline phase (polyhedral $Ba_5Si_8O_{21}$ crystals), a barium magnesium silicate crystalline phase ($BaMg_2Si_2O_7$ slats) and the residual amorphous glass phase. Small Al-rich needle-like crystals have also been observed in the range of ~ 750 - 800°C but have not been clearly identified yet.

$Ba_xSi_yO_{x+2y}$ crystal surface fraction as a function of time and temperature has been determined by SEM image analysis. The equilibrium crystalline fraction is reached very quickly above 750°C ($\sim 2\text{h}$) and $Ba_5Si_8O_{21}$ liquidus temperature in this system is in between 975°C and 1000°C . A further JMAK modelling will be applied to this system to allow the calculation of the crystallized fraction after isothermally heating at a given temperature and a given duration.

This study will be continued to fully characterize the evolution (versus time and temperature) of the other crystalline phases as well as the composition of the residual amorphous glass. A detailed knowledge of the material microstructure is necessary in order

to optimize the thermal treatment for the glass-ceramic formation and anticipate the possible microstructural evolution of the glass-ceramic seal operating in the stack. The mechanical behavior of the glass-ceramic will then be linked to its microstructure.

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