Short communication

Study on the crystallization behaviour and thermal stability of glass-ceramics used as solid oxide fuel cell-sealing materials

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ABSTRACT

Glass ceramics are commonly used as sealing materials for planar solid oxide fuel cells (SOFCs). The major requirements of stack and module builders for these materials are the stability of the coefficient of thermal expansion (CTE), excellent bonding (sticking) behaviour and the absence of volatile ingredients, which can lead to changes of the material properties and the sealing ability.

SCHOTT Electronic Packaging has developed special glasses and glass-ceramics for various solid oxide fuel cell designs and operating temperatures. The glass compositions are based on the system $MgO–Al_2O_3–BaO–SiO_2–B_2O_3$.

In this study the evaluation of the developed materials was done by high temperature aging tests for up to 1000 h, high temperature XRD-studies and Rietveld calculations, combined with scanning-electron microscope analysis. Samples of these aged samples were chemically analysed by XRD and wet chemical methods.

Results show that after thermal aging of the glasses barium silicates accompanied by barium–magnesium silicates are the major crystalline phases of the glasses. The crystal phases remain stable during high temperature aging tests, indicating a low driving force of material change. The experimental results are compared to phase diagrams by phenomenological and thermochemical considerations.

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1. Introduction

Glasses and glass-ceramics used for sealing the gas manifolds or the cell of solid oxide fuel cells (SOFCs) have to fulfill many requirements. Due to the high operating temperatures and the aggressive atmospheres, a SOFC makes high demands on the materials used, especially on the sealants.

The high operating temperatures of up to 900 °C demand glasses that do not flow, and maintain the distance between the different sealed layers. The so called "hard" glasses used for high power lamps (SCHOTT glass code 8253) could be candidates, because of their high transformation temperature (T_g) and their alkaline free composition, but their sealing temperatures are too high and the coefficient of thermal expansion (CTE) does not match the interconnect and cell materials. Moreover every glass will start crystallizing during long term operation and changes in physical properties are likely to occur. Glass-ceramics are the most widespread used sealing material for planar SOFC. They can be sealed at lower temperatures and if thermodynamic stable phases are formed no further changes in material properties occur. Another advantage is

that the so formed glass ceramic has higher chemical and mechanical stability than the base glass. The crystal phases and their amount determine the thermomechanical properties.

SCHOTT Electronic Packaging has recently developed glasses and glass-ceramics from the system $MgO–Al_2O_3–BaO–SiO_2–B_2O_3$, which are presented in this study. Materials from this system are good candidates for SOFC-sealing, because the CTE can be tailored to the interconnect materials, they can be easily sealed below 1000 °C and they show good wetting behaviour towards the interconnect materials.

The aim of this study is to analyze the crystallization behaviour in detail over time, because any change in properties could cause a potential breakdown of the overall system. Numerous papers dealt with sealing glasses for SOFC and crystallization kinetics [1–4], but only a few quantified the amount and type of crystals over time. In a second approach the experimental results were compared to phase diagrams by phenomenological and thermochemical considerations.

2. Experiments

Glasses from the system $MgO–Al_2O_3–BaO–SiO_2–B_2O_3$ are melted from technical grade raw materials in Pt-crucibles at temperatures varying between 1200 and 1550 °C. Crystalline fillers are

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Table 1
Composition (wt.%) and physical properties of studied glasses (g = glass; p.c. = partially crystalline).

Glass	1	2	3
SiO_2		25–40	
B_2O_3		5–15	
BaO		45–60	
Al_2O_3		<2	
MgO		2–15	
α_{20-300} [10^{-6} K^{-1}]	9.8 (p.c.)	9.5 (p.c.)	10.3 (p.c.)
α_{20-750} [10^{-6} K^{-1}]	n.d.	12.7 (p.c.)	13.2 (p.c.)
T_g [°C]	614	620	595
ρ [g cm^{-3}]	3.8	3.4	3.5
Sealing temperature [°C]	850	900	920
Crystallization temperature, T_x [°C]	808	760	769
Temperature at η 10^4 dPa s[a]	873	–	–
$T_x - T_g$ [°C]	194	140	175
Hemisphere temperature [°C]	853	917	944
Hemisphere temperature after 1000 h at 800 °C [°C]	n.d.	965	985

[a] Determined by rotation viscosimeter.

Table 2
Determined phases and their calculated amount after heat-treatment.

Sample ID	Exposure temperature and time	Glass	XRD-phase	Amount [wt.%]	SEM-phase
1	10 h, 810 °C	1	$Ba_5Si_8O_{21}$	21	n.d.
2	10 h, 860 °C	2	$Ba_3Si_5O_{13}$ $Ba_2Si_3O_8$	n.d.	n.d.
3	10 h, 860 °C	3	$Ba_2Si_3O_8$	41	n.d.
4	1 h, 810 °C 500 h, 800 °C	1	$Ba_5Si_8O_{21}$	22	Ba-silicate ++ Ba–Mg-silicate + Ba–Al-silicate − Glass
5	1.5 h, 860 °C 500 h, 800 °C	2	$Ba_2Si_3O_8$ $Ba_2MgSi_2O_7$ $BaMgSiO_4$ $BaAl_2Si_2O_8$	20 ca. 2 ca. 2 ca. 1	Ba-silicate ++ Ba–Mg-silicate+ Ba–Al-silicate − Glass
6	1.5 h, 860 °C 500 h, 800 °C	3	$Ba_2Si_3O_8$ secondary phase n.d.	28	Ba-silicate ++ Ba–Mg-silicate + Ba–Al-silicate − Glass
7	1.5 h, 860 °C 1000 h, 800 °C	2	$Ba_2Si_3O_8$ $Ba_2MgSi_2O_7$ $BaMgSiO_4$ $BaAl_2Si_2O_8$	20 ca. 1 ca. 1...2 ca. 0.5	Ba-silicate ++ Ba–Mg-silicate + Ba–Al-silicate − Glass
8	1.5 h, 860 °C 1000 h, 800 °C	3	$Ba_2Si_3O_8$ BaB_2O_4	28 3	Ba-silicate ++ Ba–Mg-silicate + Ba–Al-silicate −− Glass

needed to adapt the CTE of the materials and the flowing behaviour. For the development of glass ceramic composites, inert crystalline fillers are added to glass powders. Here the crystal phases do not react with the glass phase. These crystalline fillers from the BaO–SiO_2 system are synthesized in the same way as the glasses. After a homogenous melt is achieved, the melt is quenched between two water-cooled rotating steel rolls. The flakes are crushed to a particle size of $d_{50} = 10 \pm 2$ μm, $d_{99} < 40$ μm in ball mills. The grain size distribution of the powders are analysed by means of laser-light-scattering method (CILAS1064).

The milled powders are pressed to bars. These bars are then treated with their individual ceramization profile obtained for the glass and then put into furnace under air at 800 °C for up to 1000 h. These samples are further studied by X-ray-diffractometry (XRD), scanning electron microscopy (SEM) and X-ray-fluorescence (XRF) analysis. Boron is analysed by wet chemical pulping, because it cannot be detected by XRF analysis.

Hot-stage microscopy (Leitz) equipped with a picture analysis system and a furnace with a maximum operating temperature of 1600 °C is carried out to record the sinter- and flowing-curves of the samples. The glass and thermally aged samples are studied by this method. The latter is cut and polished from sintered bars into cubes with 3–4 mm edge length, whereas the initial milled powders are pressed to cubes of 3 mm edge length. All samples are heated up with a constant rate of 10 K min^{-1}. For each glass a minimum number of two experiments are performed. Calibration of the system is done with a 0.25 mm gold wire. The melting point of gold (1064 °C) is recorded with ±2 °C.

Table 3
Determined phases and their amount for 700 and 800 °C for 250 and 500 h.

Exposure time [h]	XRD-phase	Amount [wt.%]
1 h, 810 °C 250 h, 800 °C	$Ba_5Si_8O_{21}$	21
1 h, 810 °C 500 h, 800 °C	$Ba_5Si_8O_{21}$	21
1 h, 810 °C 250 h, 700 °C	$Ba_5Si_8O_{21}$	23
1 h, 810 °C 500 h, 700 °C	$Ba_5Si_8O_{21}$	23

Table 4
CTE-data on thermally treated samples.

Glass	Heat treatment	α_{20-300} [10^{-6} K^{-1}]	α_{20-750} [10^{-6} K^{-1}]
1	860 °C 1.5 h; 800 °C 500 h;	9.9	11.9
2	860 °C 1.5 h; 800 °C 500 h;	10.4	13.8
3	860 °C 1.5 h; 800 °C 500 h;	10.6	13.5

As standard substrate for the heating microscope Al_2O_3 is used, but also Crofer22 has been tested to verify, that the glasses show a good wetting behaviour on metal interfaces.

The peak-crystallization temperature (T_x) of the material is measured by DTA (Netzsch STA 409 PC/PG).

The coefficient of thermal expansion (CTE) and the glass transition temperature (T_g) of the glass and crystalline states are determined with a dilatometer (Netzsch TMA 500). The glass-ceramic composite samples are held for 10 h at temperatures of 800–860 °C before they are measured according to DIN ISO 7884-8. The measurement errors (absolute) for T_g are ±7 K and for the CTE $\pm0.2 \times 10^{-6}$ K^{-1}. The determination of the peak crystallization temperature can be measured by DTA within an error of ±3 K. The heating rate for the DTA and dilatometer measurements are 5 K min^{-1}.

High temperature XRD measurements (Panalytical XPERT PRO MPD) equipped with a furnace (Anton Paar HTK1200NK), which can reach a maximum temperature of 1200 °C. The measuring time for a scan of 2θ: 15–70° is 4 min and 30 s. The samples are measured with Cu-Kα X-ray source and the heating rate of the experiment were 2 K min^{-1} up to 940 °C, 5 K min^{-1} down to 860 °C, followed by 10 h dwell time. At room temperature an additional scan is performed to compare the high temperature diffractogram to the structure at room temperature. The amount of crystalline phase is calculated using Rietveld refinement method using ZnO and CaF_2 as crystalline standards.

Additional viscosity measurements with a rotation viscometer (self construction) are also carried out. The viscosity of the more rapid crystallizing glasses 2, and 3 cannot be measured by this method. However the hot stage microscopy data can be used to correlate the characteristic temperatures with the viscosity of the material. The viscosity at the hemisphere temperature equals $\log \eta = 4.6 \pm 0.1$ dPa s [5].
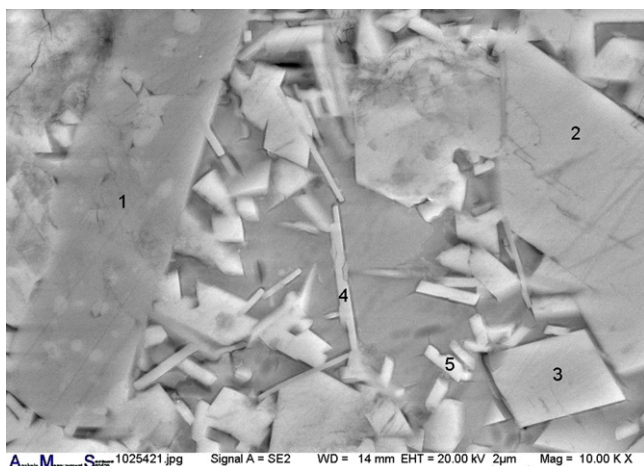

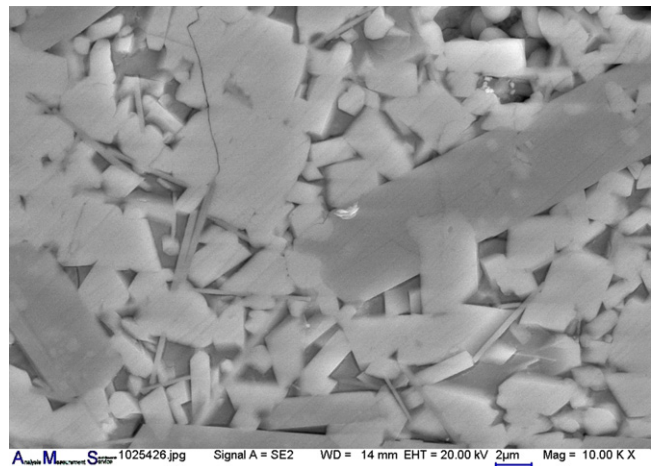**Fig. 1.** Microstructure of glass 1 (sample 7, Table 2).

Fig. 2. Microstructure of glass 2 (sample 8, Table 2).

3. Results and discussion

3.1. Glass characterization

Information on the composition (in wt.%) and main physical properties of the studied glasses are listed in Table 1. The listed glasses are only an extract of the available SOFC sealing glasses from SCHOTT.

The glass-ceramic composites 2 and 3 are derived from the glass ceramic 1 by adding crystalline fillers up to 25 wt.% to the glass in order to modify the thermal expansion coefficient and the viscosity of the material. The preferred sealing temperatures of the glasses are between the softening and the hemisphere temperatures. The flowing and melting regions of the thermal treated samples are also added in Table 1. It can be seen that after a period of 1000 h at 800 °C the hemisphere temperatures and also the flowing temperatures of samples 2 and 3 increases. During the crystallization the amorphous glass phase diminishes, therefore the melting and flowing regions are very sharp, similar to a crystalline material which has a defined melting point.

The influence of grain size on sintering and flowing behaviour was studied with glass 1 using two different grain sizes $d_{50} = 9$ μm, $d_{99} < 50$ μm (SCHOTT grain size K3) and finer grain size with $d_{50} = 4$ μm, $d_{99} < 25$ μm (SCHOTT grain size K6). Only a slight difference on the sintering behaviour was detected and no influence on the crystallization temperature. This gives evidence that the crystallization behaviour is not driven by surface crystallization.

All glasses have a large difference $T_x - T_g$, meaning that they are not rapid crystallizing glasses, and the softening and wetting takes place prior to the start of crystallisation.

3.2. Phase formation after heat treatment

In order to gain more insight into the crystallization kinetics the selected glasses were exposed to different heat and exposure treatments. The determined phases and their amount in weight percent for the glasses are summarized in Table 2. The HT-XRD study reveals that the glasses start to crystallize at 750 °C, forming mainly barium silicate-phases. The main crystalline phases remain unchanged during the exposure time for the glasses. Due to texture effects the classification of the XRD phases are difficult, especially in low amounts, but together with SEM analysis the phases can be correlated and relative amount of the phases are indicated in the column: "SEM-phase" in Table 2.

A boron containing phase crystallizes in low amounts in the glass 2 tempered for 1000 h. This is advantageous because boron

Table 5
Major phase relation of the investigated glasses and their XRD determined phases.

Glass	Major phase relations		XRD (see also Table 2)
2	$Ba_2Si_3O_8$, $BaMg_2Si_2O_7$, $Ba_2MgSi_2O_7$, $Ba_3B_3Si_2$		*After 1000 h thermal treatment*: $Ba_2Si_3O_8$, $Ba_2MgSi_2O_7$, $BaMgSiO_4$
3	$Ba_2Si_3O_8$, BaB_2O_4, $BaMg_2Si_2O_7$, $Ba_3B_6SiO_{16}$		$Ba_2Si_3O_8$, BaB_2O_4
1	*Quaternary* $Ba_2Si_3O_8$, $BaSi_2O_5$, $Ba_3B_6SiO_{16}$, $BaMg_2Si_2O_7$	*Quasi-Binary* $Ba_5Si_8O_{21}$	$Ba_5Si_8O_{21}$

integrated in the crystal phase forms a stronger bond than in the residual glass phase, therefore volatilization of boron is less likely to take place. The melting point of the BaB_2O_4 phase is above 1100 °C [6].

Glasses enriched in boron can easily be corroded by humid gases and evaporation of boron species further depletes the glass of boron at high temperatures. The boron content (B_2O_3) was analysed for samples 7 and 8, which have been tempered for 1000 h. The deviation compared to the synthesis was below 5%.

It is noteworthy that for the glass 1 only one crystalline phase is predominant of which theoretical 70 wt.% can be formed.

Because solid oxide fuel cells do not operate at constant temperatures it has been tested whether there are changes in crystalline phases and their content for samples tempered at 700 °C and 800 °C. These temperatures correspond to a lower and standard operating temperature. The tests were performed using the glass 1, but no changes were observed (Table 3).

The microstructure of the glasses 2 and 3 after heat treatment for 1000 h are shown in Figs. 1 and 2. The barium silicate crystals have a rhombic shape (1 and 2 in Fig. 1) and are accompanied by barium magnesium silicates (3 in Fig. 1) which show preferred crystal growth in one direction of space. These crystal-laths, though less abundant, grow up to 30 μm in length.

In between barium silicates, needles of barium-alumino-silicates (4 and 5 in Fig. 1) and remaining residual glass phases can be found. The barium silicates appear to crystallize first, because some of the crystals are embedded in the barium–magnesium-laths (Fig. 2).

3.3. Dilatometric measurements of exposed samples

Dilatometric measurements were carried out on 500 h thermally exposed samples to determine if any changes due to crystal phases or alterations of the overall glass compositions after heat treatment occur. The results are given in Table 4. The CTE of glass 1 remains unchanged taken the measurement errors into account. A slight increase in the CTE for the glasses 2 and 3 can be explained by further crystallization of barium silicate phases, having a higher CTE than the residual glass matrix.

3.4. Phenomenological thermochemistry

The thermal behaviour and linked phase transformations were additionally studied by phenomenological thermochemistry. The major phase relations in the according phase diagrams of the glasses 2, 3, and 1 were investigated manually. Commercial software packages, e.g. FactSage [7] do not succeed due to the lacking data of both, basic data for barium compounds and solution models of containing phases. However, simple phase diagrams, e.g. [6], cannot visualize the phase relations of the multi-component glass

sealing in one convenient diagram for the benevolent reader. In order to overcome these hurdle the stable phases for each binary and ternary main component were evaluated and the relations are summarized.

The relevant phase diagrams for the discussed glasses are (i) BaO–SiO_2, (ii) BaO–B_2O_3–SiO_2, (iii) BaO–Al_2O_3–SiO_2, and (iv) MgO–BaO–SiO_2.

For all glasses ratio of the components in each pseudo-ternary system was calculated and the composition point at constant pressure ($p = 1$ atm) and constant temperature ($T = 800$ °C) was identified in the system. The phase relations which are found for the three glasses that are shown in Table 5.

For the sealing glass 2 the detected XRD phases after long heat treatment are the same as the phases of the sub ternary triangle or sub-quaternary tetrahedron, respectively. This is evidence that after the transformation into the phases B_2S_3 ($B = BaO$; $S = SiO_2$) and BM_2S_2 ($M = MgO$) there is no driving force for further material change. The fact that not all phases of the phase diagram are found in XRD measurements is due to both, experimental resolution of the equipment and compositional dominance of the two detected phases. The same phenomenon is observed for the glass 3, which consists of the phases B_2S_3 and BB (BaB_2O_4). Again, the glass sealing should be very stable against aging, because of the lacking driving force for material change.

Only glass 1 seems to deviate from the known phase diagrams. Regarding the total composition, the glass lies in the same sub-polyhedra. Reducing the composition to the binary BaO–SiO_2 only B_5S_8 is found as the stable equilibrium phase. The only explanation, which can be concluded is, that there must be a missing sub-triangle in the system BaO–B_2O_3–SiO_2, namely B_5S_8–B_2S_3–$B_3B_3S_2$.

4. Conclusions

Glass ceramics from the system MgO–Al_2O_3–BaO–SiO_2–B_2O_3 have been investigated and their thermal properties and crystallization studied. The main crystalline phases remain unchanged during an exposure time of 1000 h, which is further verified by dilatometric measurements at the exposed samples. Barium silicate, namely $Ba_2Si_3O_8$ is the dominant phase determined by XRD-measurements for the glasses 2 and 3. This is consistent with the phase relations determined from the phase diagrams, indicating again a low driving force for material change. For the glass 1 the main crystalline phase is $Ba_5Si_8O_{21}$, which has been tested to be stable throughout the typical operating range of SOFC between 700 and 800 °C. After crystallization the wetting and flowing region of the materials is increased by 40–50 °C compared to non crystallized materials. The shown properties, especially the high temperature and CTE-stability over time, make the introduced SCHOTT glass-ceramics excellent materials for use as SOFC sealants.

Acknowledgement

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