Crystallization and void formation in ZnO–B₂O₃–SiO₂–MgO sintered solder glasses

JEONG SEOG KIM, CHAE IL CHEON
Department of Materials Science and Engineering, Hoseo University, San 29-1 Sechul-Ri, Baebang-Myoun, Asan, Chungcheongnam-Do 336-795, Korea

The evolution of crystallization and porosity changes with firing temperature were studied in ZnO–B₂O₃–SiO₂–MgO glasses. Those glasses presintered at 610 °C to a low porosity were crystallized in the temperature range of 690–870 °C. The glasses were crystallized by a surface crystallization mechanism. The porosity increased with the crystallization temperature. In the temperature range of 710–790 °C, several crystalline phases, such as 3ZnO–B₂O₃, willemite (2ZnO–SiO₂), 5ZnO–2B₂O₃, and another form of zinc silicate (2ZnO–SiO₂), produced at relatively low temperatures, were produced, while above 800 °C only the 2ZnO–SiO₂ phase co-existed with a glass phase. Only an observed density difference between the glass and the crystallized glass cannot be attributed to the void formation during the crystallization reaction. Due to the crystallization the composition of the remaining glass around the crystalline phases is expected to change. The depletion of a certain component in the remaining glass, probably the SiO₂ due to the production of the 2ZnO–SiO₂ phase, might result in the increase in the vapour pressure of the remaining glass and lead to the observed increase in porosity. Below 800 °C, at which temperature the crystallization rate is fast and only a small amount of the glass phase remained, the porosity remained constant after the completion of the crystallization. Contrarily at 860 °C the porosity continuously increased with firing time.

1. Introduction

The solder glasses that crystallize in the ZnO–B₂O₃–SiO₂–MgO system are used in the passivation of semiconductor power devices and also the seals for metal leads with a low thermal expansion coefficient, such as Mo, kovar, and invar [1, 2]. For passivation purposes the glass powder of ZnO–B₂O₃–SiO₂ is deposited, using one of several methods, onto the surface of devices such as transistors, diodes, and thyristors, as a 10–20 μm thick film. The deposited layer when fired at 650–750 °C provides the devices with a resistance to humidity and also electrical insulation. The crystallization behaviour and the characteristics of the interface between the glass layer and the device has been reported in several papers. Murakami *et al.* [3] have reported that a passivation glass with a composition of 65ZnO–25B₂O₃–12SiO₂ (wt %) could be crystallized in the temperature range of 690–730 °C. At relatively low temperatures (~710 °C) a primary crystallization occurred as

$$3ZnO + B_2O_3 \rightarrow 3ZnO–B_2O_3 \qquad (1)$$
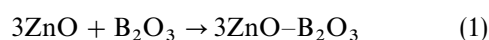
At a relatively high temperature (~730 °C), the 5ZnO–2B₂O₃ phase was produced by an exothermic reaction as follows

$$3ZnO–B_2O_3 + 2ZnO + B_2O_3 \rightarrow 5ZnO–2B_2O_3 \qquad (2)$$
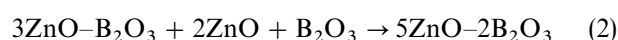
The crystallite size and firing temperature are important parameters if the glass is to be optimally controlled to allow adaption to the devices.

On the other hand, the required properties for a metal seal are different from the passivation glass. Hence glass composition and firing characteristics of the metal seal are somewhat different from the passivation glass. The cathode support assembly in a TV-cathode ray tube is a typical application case of the ZnO–B₂O₃–SiO₂–MgO glass for the sealing of low thermal expansion metals. The manufacturing procedure for this type of article is as follows. A small tablet with holes is pressed from the glass powder and presintered in the temperature range of 600–680 °C. After assembling the sintered tablets with metal leads and case, sealing is conducted in the temperature range of 750–820 °C. Since the cathode support assembly is operated at a relatively high temperature (500–700 °C) and high vacuum (1.333×10^{-5} Pa), the glass should have a thermal and structural stability in addition to electrical insulation. Therefore, crystallization and fired density can be important parameters affecting the performance of the sealed article. However, the crystallization and firing behaviours of ZnO–B₂O₃–SiO₂–MgO glass used for metal sealing are not clearly understood.

In the production of sintered glass-ceramics a nonporous sintered body is generally the most desired characteristic. Unfortunately, usually, surface

crystallization inhibits sintering to complete densification. Morell *et al.* [4] and Clark *et al.* [5] have reported that the surface crystallization in cordierite glass ceramics limited the sintering temperature to a narrow range. Rabinovich *et al.* [6] showed that a glass that is susceptible to surface crystallization at relatively low viscosity can be successfully sintered either before the crystallization or simultaneously with the crystallization. They suggested that a glass with a slow crystallization rate could form a dense sintered body. The sintering temperature of the $ZnO-B_2O_3-SiO_2-MgO$ metal sealing glass is very low ($\sim 601\,°C$) as compared to the crystallization temperature ($700-830\,°C$). In this glass system a near full density can be obtained by sintering at $610-680\,°C$. However when the sintered glass containing a low porosity is crystallized at higher temperatures, the porosity significantly increases with temperature.

The formation of voids during the crystallization reaction in a dense body has also been reported on a calcium–phosphate glass which has been studied as a substitute biomaterial for bones or teeth [7, 8]. The difference in the densities between the original glass and the resulting crystalline phase (β-$Ca(PO_3)_2$) was attributed to void formation. The size and distribution of these voids formed during crystallization varied with the crystallization rates in the calcium phosphate glass. In this study the characteristics of a $ZnO-B_2O_3-SiO_2-MgO$ glass are analysed as a function of the crystallization. The differences in the crystallization behaviours and void formation mechanisms between the $ZnO-B_2O_3-SiO_2-MgO$ and the calcium–phosphate glasses are discussed.

2. Experimental procedure

Two types of glass powders were used: a commercially available sealing glass (Nippon Electric Glass Co., product name: ZF-4/K) and glasses prepared in the authors' laboratory. The specification of the commercial glass is summarized in Table 1. The compositions of the prepared glasses in wt % are as follows: $59ZnO-28.5B_2O_3-10SiO_2-2.5MgO$ (glass A) and $54.5ZnO-30.5B_2O_3-11SiO_2-4.0MgO$ (glass B). The appropriate stoichiometric amounts of ZnO, B_2O_3, SiO_2, and MgO were mixed and then melted at $1300\,°C$ in air. The glass melt was poured into cold water. Then the water quenched glass frit was ground in a ball mill. The glass powder was mixed with a binder and then pressed at $200\,kg\,cm^{-2}$ into cylinders of about 3 mm in height and 10 mm in diameter. The
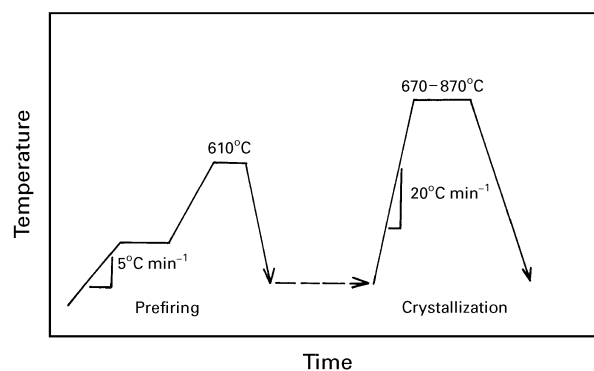

Figure 1 Firing schedule for the prefiring and crystallization.
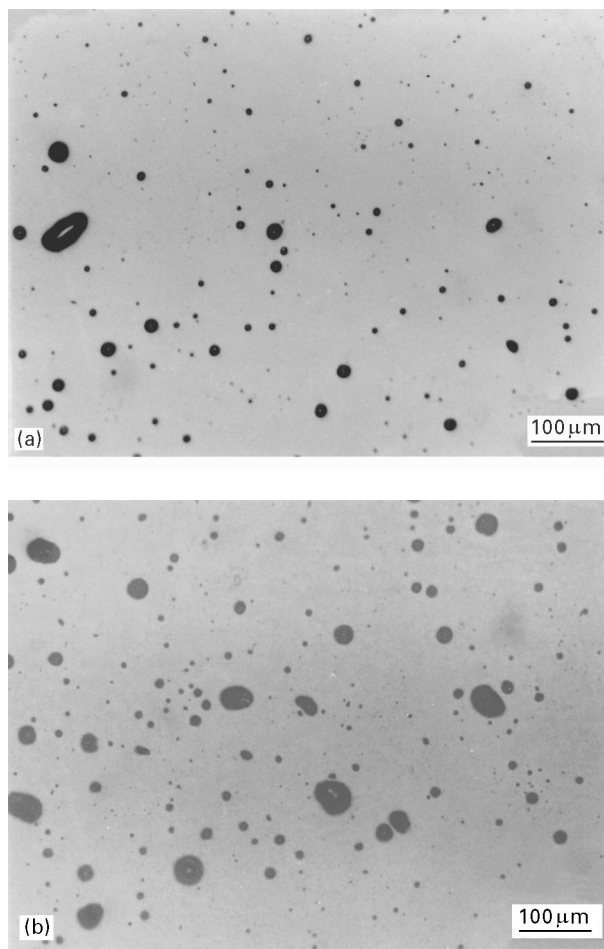

Figure 2 Optical microstructures of the glass A (a) prefired at $680\,°C$ for 30 min; (b) crystallized at $760\,°C$ for 50 min.

firing schedules for the glass compacts are shown in Fig. 1. The glass compacts presintered at $610\,°C$ for 30 min in air were crystallized at higher temperatures of $670-870\,°C$. In order to study the effect of firing atmosphere on the fired density some of the glass compacts were prefired in O_2 and Ar at $610\,°C$ for 30 min and then they were crystallized at $760\,°C$ for 50 min in air. Scanning electron and optical microscopes were used for the microstructural observations on polished surfaces. The X-ray diffractometer used for analysing the crystalline phases was a Shimadzu DX-1 with a Cu target. The porosity of the fired specimens was measured by the point counting

TABLE I Properties of the commercial glass ZF-4/K

Composition	$51.8ZnO-34.1B_2O_3-10.6SiO_2-3.5MgO$
Density (glass) ($g\,cm^{-3}$)	3.64
Softening point (°C)	661
Working point (°C)	820
Thermal expansion coefficient (per °C)	51.2×10^{-7}
Glass transition temperature T_g (°C)	560

method. An apparent density was measured using the Archimedes' principle on five samples at each firing condition.

3. Results and discussion

The microstructure of glass A presintered at 610 °C is presented in Fig. 2(a). The black and spherical regions are pores. The figure shows a dense sintered body with a low porosity. When the presintered glass A is crystallized at 760 °C, the porosity significantly increases as is shown in Fig. 2(b). Fig. 3(a–c) shows the measured variation of the porosity, apparent densities, and the number of pores per unit area with crystallization temperatures in the commercial glass ZF-4/K. The porosity increased with the firing temperature, and consequently the apparent density decreased with the temperature. Both the number of pores per unit area
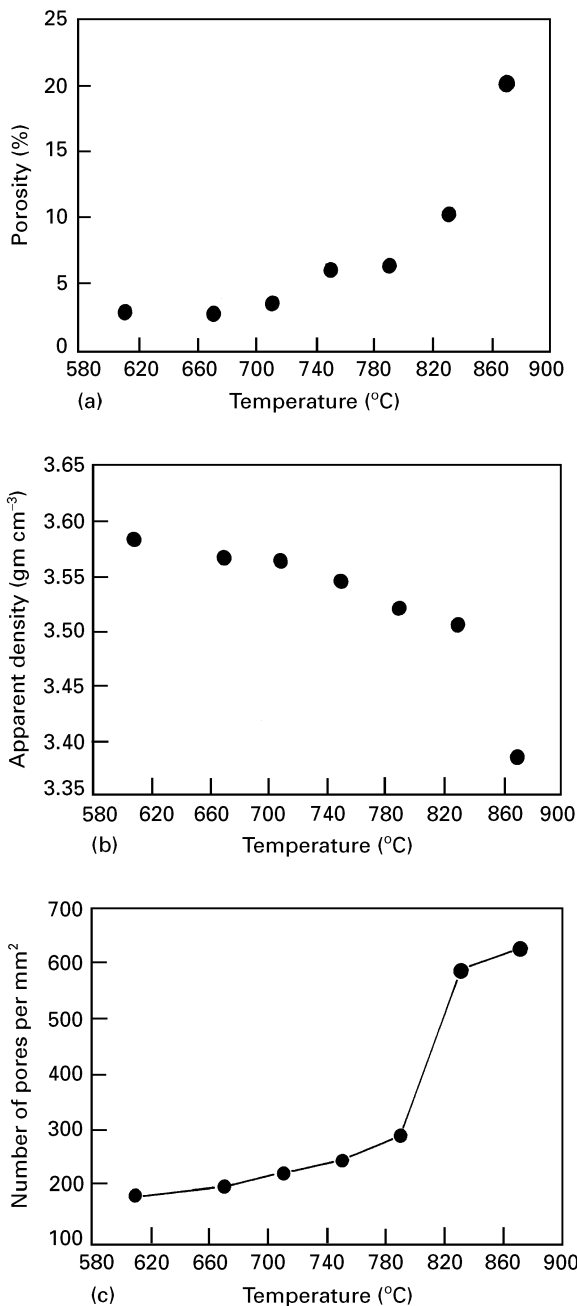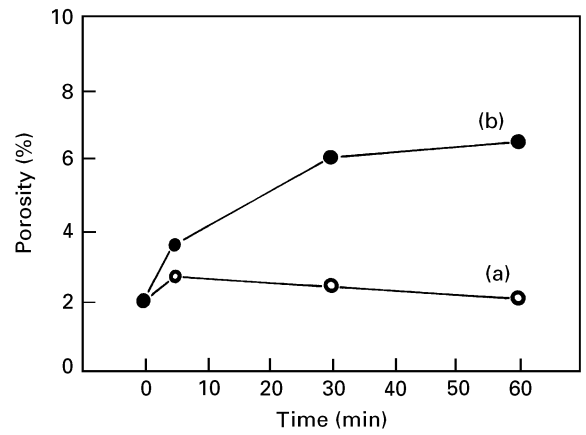
Figure 4 Porosity change with firing time at (a) 690 °C and (b) 760 °C in the ZF-4/K.

and porosity increased steeply at about 830 °C. Fig. 4 shows the variation of the porosity with time at 690 °C and 760 °C in the ZF-4/K glass. At 690 °C, a temperature at which the crystallization rate is very slow, no significant change in the porosity was observed until after 60 min. In contrast, at 760 °C the porosity steeply increased upto 30 min and then remained constant.

The increase in porosity with temperature in the $ZnO-B_2O_3-SiO_2-MgO$ glasses can be attributed to several factors. Firstly, the volume of the pores containing insoluble gases trapped during the presintering at 610 °C could expand during the second firing at higher temperature [9]. Secondly, due to the crystallization of the glass the true density of the glass could be changed. Finally, a glass phase with a high vapour pressure could be produced during the crystallization reaction or at high temperature. In order to test the possibility of the volume expansion of the pores thought to contain trapped insoluble gases, some glass compacts were presintered at 610 °C in O_2 and Ar instead of air. Then the presintered glasses were crystallized at 760 °C for 50 min in air. During the presintering treatment the glass compacts were binder-burnt out at 350–450 °C for 2–3 h in air. The porosity of the presintered glass in O_2 was lower (about 2 vol %) than that sintered in Ar (about 4 vol %). Since the solubility and the diffusivity of Ar in the glass is expected to be much lower than those of O_2, the expected lower porosity in O_2 was observed. However, regardless of the prefiring atmosphere the porosity after the crystallization at 760 °C increased to about 4.6 and 6.4 vol % in O_2 and Ar respectively.

Fig. 5 shows a scanning electron micrograph of the ZF-4/K crystallized at 760 °C for 30 min. The smooth surface region indicated by the arrows is a non-crystallized glass phase and the rest is crystallized. It can be seen that after 30 min the crystallization is nearly completed. Comparing to the porosity change with time at 760 °C in Fig. 4, it can be found that during the crystallization the porosity increased, and after the completion of crystallization the porosity remained constant at 760 °C. The evolution of the phase composition of the ZF-4/K glass with firing temperature as determined by X-ray diffraction is shown in Fig. 6. The prefired glass began to crystallize at about 690 °C
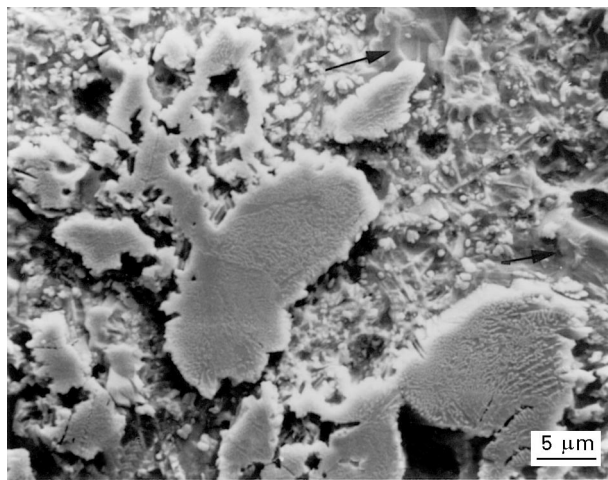
Figure 3 Variations of (a) porosity (b) apparent density (c) number of pores per unit area with firing temperature in the ZF-4/K glass.

1577

Figure 5 Scanning electron micrograph of the ZF-4/K glass fired at 760 °C for 30 min (etched by picric acid).

Figure 7 Surface crystallization of the water quenched frit of glass A prefired at 680 °C for 50 min and then crystallized at 780 °C for 1 h.
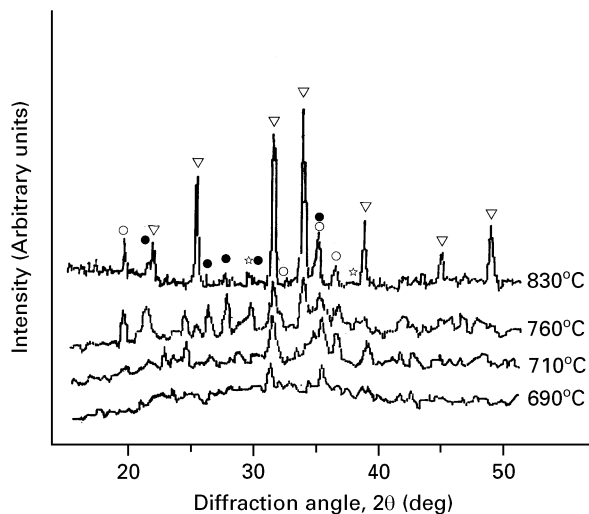

Figure 6 X-ray diffraction patterns of the ZF-4/K glass crystallized for 30 min at (a) 690 °C, (b) 710 °C, (c) 760 °C and (d) 830 °C. Key: (●) $3ZnO-B_2O_3$ (▽) $2ZnO-SiO_2$ (willemite), (☆) $5ZnO-2B_2O_3$ and (○) $2ZnO-SiO_2$.

Figure 8 Crystallization rates of the glasses A and B at 780 °C.

and small amounts of an unidentified crystalline phase were produced. At 760 °C the glass–ceramic is mainly composed of $3ZnO-B_2O_3$, willemite ($2ZnO-SiO_2$), $5ZnO-2B_2O_3$, and zinc silicate ($2ZnO-SiO_2$). When the firing temperature is increased, the willemite phase becomes the dominant phase, and at 830 °C only the $2ZnO-SiO_2$ phase co-exists with a glass phase. This temperature corresponds to the point at which the porosity begins to increase abruptly as is shown in Fig. 3.

Voids can be produced during crystallization when a glass shows a surface crystallization behaviour. In the calcium phosphate glass the densities of the original glass and resulting crystallized glass were $2.72\ g\ cm^{-3}$ and $2.84\ g\ cm^{-3}$ respectively. In this glass the apparent volume was nearly constant during and after the crystallization, because a crystallized rigid shell formed from the free surface of the glass body in the early stage of crystallization. Consequently, the voids, having a volume corresponding to the density difference, were produced as a result of the crystallization. Figs. 7 and 8 show the crystallization behaviour
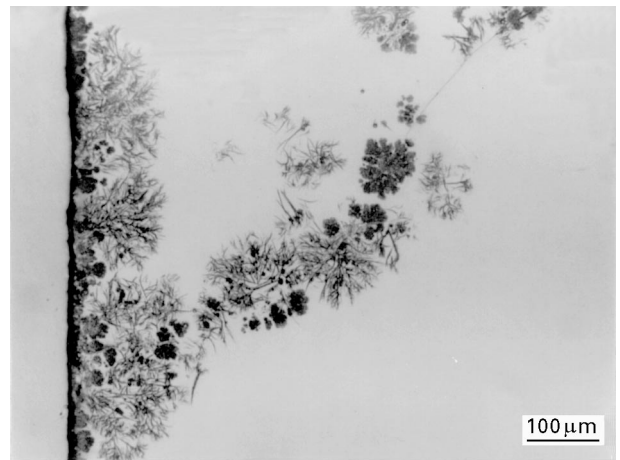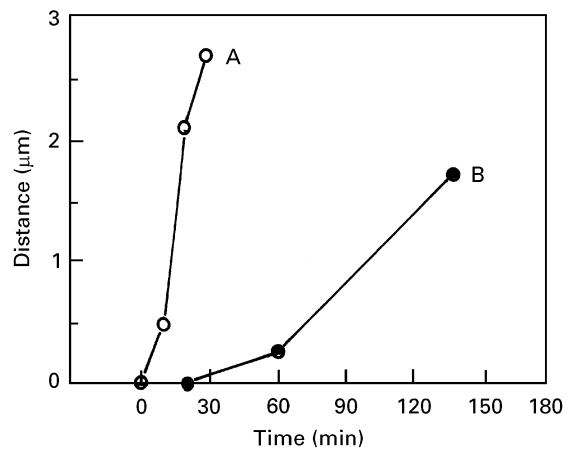
of the A and B glasses. Water quenched glass frits with particle sizes of about 1–5 mm were presintered at 680 °C without ball milling, then the sintered glasses were crystallized at 780 °C for varying time periods. The crystalline phases grew from the free surface and the boundaries between glass frit particles as is shown in Fig. 7. The average distances of the crystallization fronts from the free surface or the interfaces between glass particles were measured. Although showing quite different crystallization rates, both of the glasses showed surface crystallization behaviour. The true density of the ZF-4/K glass is $3.64\ g\ cm^{-3}$ and those of $3ZnO-B_2O_3$ and willemite ($2ZnO-SiO_2$) are $4.17\ g\ cm^{-3}$ and $4.10\ g\ cm^{-3}$ respectively. As discussed for the calcium phosphate glass case the surface crystallization can prevent the volume shrinkage of the glass during the crystallization in the $ZnO-B_2O_3-SiO_2-MgO$ glasses. The difference in the densities between the crystallized and non-crystallized glasses can lead to the formation of voids observed in this glass similarly to the calcium phosphate glass. However, in the range of 830–870 °C in which only the $2ZnO-SiO_2$ phase coexists with the glass phase, the porosity increased more steeply with temperature, even though the amount of glass phase increases with the temperature. Moreover, at 860 °C the porosity was observed to increase steadily with time upto 4 h which

is contrary to the behaviour below 800 °C. Hence only the density difference between the glass and the glass–ceramics cannot be attributed to the formation of voids in the glasses with an increase in the firing temperature. In these glasses, as shown in Fig. 6, several crystalline phases are produced and the compositions of the crystalline phases are quite different from the nominal composition of the original glass. By the formation of the crystalline phases the composition of the remaining glass matrix around the growing crystalline phases is expected to be changed. Especially, when the $2ZnO–SiO_2$ phase is formed, the SiO_2 content would be depleted in the remaining glass and the physical properties of the remaining glass, such as vapour pressure and viscosity become modified from those of the original glass. If the vapour pressure of the remaining glass increased, the porosity would significantly increase as is observed in these results. However, at temperatures below 800 °C the crystallization rate is very fast and several crystalline phases coexist possibly with a small amount of glass phase. Therefore, the porosity could not increase further after the completion of crystallization.

4. Conclusion

In general a crystallized glass has a slightly higher density than that of the original non-crystallized glass. The density difference between the two glass states can lead to the formation of voids, especially when the apparent volume of the glass remains nearly constant during a surface crystallization. In the $ZnO–B_2O_3–SiO_2–MgO$ sealing glass the crystalline phases are produced by a surface crystallization mechanism and the crystalline phases are denser than the original glass. Therefore, the density difference between the glass and the crystallized glass could be attributed to the formation of voids during the crystallization. However, the porosity increases even more steeply in the temperature range of 830–860 °C in which only the zinc silicate ($2ZnO–SiO_2$) and a glass phase co-exist. In this temperature range the crystallinity is lower as compared to that below 800 °C. This observation implies that only the density difference between the original glass and the crystalline phases cannot successfully explain the porosity increase during the crystallization reaction. It appears that the formation of the crystalline phases, especially the $2ZnO–SiO_2$ could leave the remaining glass deficient in SiO_2 content. Therefore, the vapour pressure of the remaining glass might increase and lead to the steep increase in the porosity. However, in the temperature range of 730–800 °C, the amount of remnant glass phase is expected to be very small, since several crystalline phases are produced, such as $3ZnO–B_2O_3$, willemite ($2ZnO–SiO_2$), $5ZnO–2B_2O_3$, and zinc silicate ($2ZnO–SiO_2$). Hence the porosity could remain constant after the completion of the crystallization reaction.

References

1. Y. MISAWA, H. HACHINO, S. HARA and M. HANAZONO, *J. Electrochem. Soc.: Solid-State Sci. and Tech.* **131** (1984) 359.
2. Y. MISAWA, *ibid.* **131** (1984) 2618.
3. S. MURAKAMI, K. MIYATA, M. TSURUOKA and Y. KOBAYASHI, *ibid.* **134** (1987) 2293.
4. R. MORELL, *Proc. Br. Ceram. Soc.* **28** (1979) 53.
5. T. J. CLARK and J. S. REED, *J. Amer Ceram. Soc.* **69** (1986) 837.
6. E. M. RABINOVICH, *J. Mater. Sci.* **20** (1985) 4259.
7. A. WATANABE, Y. IMADA and S. KIHARA, *ibid.* **69** (1986) c31.
8. A. WATANABE, M. MITSUDOU, S. KIHARA and Y. ABE, *ibid.* **72** (1989) 1499.
9. J. -J. KIM, B. -K. KIM, B. -M. SONG and D. Y. KIM, *ibid.* **70** (1987) 734.