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The effect of additives on the crystallization and sintering of $2MgO–2Al_2O_3–5SiO_2$ glass–ceramics

YUN-MO SUNG*
Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706, USA

Crystallization and sintering behaviour of three cordierite ($2MgO–2Al_2O_3–5SiO_2$) glasses containing different amount of additives were investigated and compared by using differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and the Archimedes method. The stoichiometric $2MgO–2Al_2O_3–5SiO_2$ (MAS) glass and the $2MgO–2Al_2O_3–5SiO_2$ glass containing 3 wt% of B_2O_3 and 3 wt% of P_2O_5 (MASBP) showed two exotherms (one for μ-cordierite formation from a glass and the other for α-cordierite formation from the μ-cordierite phase), whereas the $2MgO–2Al_2O_3–5SiO_2$ glass containing 2 wt% of B_2O_3, 2 wt% of P_2O_5, and 2 wt% of TiO_2 (MASBPT) showed only a single exotherm representing α-cordierite formation. By using Kissinger, Augis–Bennett, Ozawa, and modified Kissinger methods, the activation energy values for α-cordierite formation in the MASBP and MASBPT glasses were determined as 310 ± 6 and 326 ± 13 kJ mol^{-1}, respectively, whereas that in the MAS glass was determined as 868 ± 5 kJ mol^{-1}. The MASBPT glass showed the lowest peak temperature value for α-cordierite formation (980 °C) amongst the three glasses. Both the MASBP and MASBPT glasses showed excellent sintering behaviour (> 99.7% of theoretical density).

1. Introduction

Glass–ceramics are crystalline materials which can be formed by controlled crystallization heat treatments of proper glasses. Most of them have some unique property such as translucency, high strength, and very low and uniform thermal expansion. They have very fine (~1 μm) and randomly oriented crystals with a few per cent of the residual glass [1].

Cordierite ($2MgO–2Al_2O_3–5SiO_2$) is a glass–ceramic that is well-known for its good mechanical properties (strength of ~250 MPa and modulus of ~150 GPa), a low dielectric constant (~5), and a low thermal expansion coefficient ($\sim 2 \times 10^{-6}$ per °C) [2]. These excellent properties allow cordierite to be used for high-temperature structural applications [3–7] and semiconductor packaging [8, 9].

The preparation of cordierite glass–ceramics by sintering glass powders followed by crystallization heat treatments has been previously studied. Rabinovich [10] examined the sinterability of the cordierite glasses. All of the glasses containing TiO_2 as a nucleating agent, crystallized prematurely and showed poor sintering except those glasses containing Na_2O. Panda *et al.* [11] studied the effect of heating rate on the sintering and crystallization of the cordierite glasses. They reported that by increasing the heating rate crystallization can be delayed so that cordierite glasses sinter to full density. Rudolph *et al.* [12] studied the sintering behaviour of P_2O_5-modified cordierite and found that the porosity exhibits a distinct minimum for a heating rate of 15 °K per min. They indicated that this effect is based upon a variation of the effective sintering interval ranging from T_g (glass transition) to T_o (onset temperature of crystallization). Knickerbocker *et al.* [9] studied the sintering behaviour of the cordierite glass–ceramics with and without B_2O_3 and P_2O_5 addition. They found that off-stoichiometric cordierite glasses have lower viscosity and slow crystal growth rate, resulting in good sinterability. Also, they found that even a small amount of B_2O_3 and P_2O_5 addition is effective to control sintering and crystallization of a cordierite glass.

Rankin and Merwin [13], and also Geller and Insley [14] have reported that cordierite has a stable high-temperature phase (α-cordierite) and a metastable low-temperature phase (μ-cordierite). Toropov and Sirazhiddinov [15] suggested that the formation of the metastable phase (μ-cordierite) might be the result of chemical heterogeneity in the structure of the original glasses. They found that a heat treatment above 1100 °C caused decomposition of the metastable phase.

It is well known that TiO_2 additions can have a remarkable influence on the crystallization of

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* *Present address*: Department of Materials Science and Engineering, Daejin University, Pochun-kun, Kyungki-do 487-800, Korea.

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$MgO–Al_2O_3–SiO_2$ systems. Maurer [16] studied the mechanism of crystallization in $MgO–Al_2O_3–SiO_2–TiO_2$ glass using light scattering and explained the role of TiO_2. He found that the crystallization of TiO_2-rich regions is caused by an emulsion within the vitreous body. Toropov *et al.* [17] studied the effect of TiO_2 addition on the phase transformation of a cordierite glass. They reported that the addition of 15 wt % TiO_2 caused a decrease in the amount of μ-cordierite and a narrowing of the "temperature interval of existence" resulting from the formation of magnesium and aluminum titanates. DeVekey and Majumdar [18] found that TiO_2 and a mixture of TiO_2 and ZrO_2 in amounts ranging from 10–12 wt % could be employed to produce good quality glass–ceramics. They examined the phenomenon of glass-in-glass separation as a precursor to controlled crystallization using electron microscopy.

The purpose of this research is to analyse the combined effects of B_2O_3, P_2O_5, and TiO_2 additions on the sintering and crystallization behaviour of cordierite glass–ceramics. In detail, the focus of this study is not only to enhance the sintering of cordierite glass–ceramics by B_2O_3 and P_2O_5 addition, but also to decrease the crystallization temperature of cordierite glass–ceramics by TiO_2 addition to enable engineering applications such as substrate fabrication for semiconductor packaging, to become feasible.

2. Experimental procedure

High purity powders of MgO, Al_2O_3, SiO_2, B_2O_3, P_2O_5, and TiO_2 were used to produce cordierite glasses. The chemical compositions of each glass are listed in Table I. B_2O_3 (3 wt %) and P_2O_5 (3 wt %) were added to the stoichiometric composition of cordierite in order to enhance sinterability. B_2O_3 (2 wt %), P_2O_5 (2 wt %), and TiO_2 (2 wt %) were added to the stoichiometric cordierite in order to enhance sinterability and also to decrease the crystallization temperature. The chemicals were well mixed by zirconia-ball milling (YTZ Zirconia-ball media, Tosoh USA Inc., Atlanta, GA, USA). The glasses were prepared in a 50-ml platinum crucible using an electrical resistance furnace (DT-31-HT, Deltech Inc., Denver, CO, USA) in an air atmosphere. To homogenize the melt the mixtures of the chemicals were held at 1600 °C for 2 h. The platinum crucible containing the glass melt was removed from the furnace and quenched in distilled water to obtain a clear glass. Pouring the glass melt from the crucible was impossible due to the high sample viscosity and difficulty in controlling the temperature. The glass fragments were well dried in an oven and were hand-ground using an alumina mortar and pestle. The ground powders were screened by a 325-mesh sieve and then ball-milled in a rotating milling machine with the same zirconia balls used previously in methyl alcohol. After a 6 h-milling with a ball-milling speed of approximately 180 rpm the size of the glass particles ranged from 5–10 μm. No zirconia contamination was detected by energy dispersive X-ray spectroscopy (EDX, TN-55000, Noran Co., Middleton, WI, USA) analysis. The crystallinity and crystallization temperatures of these glass powders were investigated by using wide angle X-ray diffraction, (Nicolet Stoe Transmission/Bragg-Brentano, Stoe Co., Germany) and differential thermal analysis, (Perkin-Elmer DTA 1700, Norwalk, CT, USA). The DTA measurements were performed using 65 mg of glass powders in a platinum crucible in an air atmosphere with heating rates of 3, 5, 10, 20, 40, and 80 °C per min from 600–1400 °C. The DTA results were further analysed to obtain the crystallization mode and the activation energy values for crystallization of each glass by using the Kissinger, modified Kissinger, Augis–Bennett, and Ozawa methods. The ball-milled powders mixed with an organic binder (a mixture of poly-vinyl- butyral and acetone) were cold-pressed in a 6.35 mm-diameter cylindrical stainless steel die under pressure of 20.7 MPa. To obtain a rapid heating effect for good sintering these small pellets were put into the electrical resistance furnace which was already set at the sintering temperatures pre-selected from DTA measurements. The sintered pellets were further heat treated for crystallization. Sintering and crystallization of the glass–ceramic pellets were examined by using SEM (Jeol SEM 35-C, Jeol, Japan), Archimedes method, and XRD.

3. Results and discussion

The XRD results for the three different glasses showed clear non-crystallinity. DTA results from these four glasses are shown in Figs 1–3. The MAS and MASBP glasses showed two crystallization peaks representing μ-cordierite formation at low temperature and α-cordierite formation at higher temperature, whereas the MASBPT glass showed a single peak representing α-cordierite formation. This was readily confirmed by the XRD measurements on each glass. The titanate formation or phase separation caused by TiO_2 addition would lead to α-cordierite phase formation directly from a glass phase. This result is well supported by the work of Toropov *et al.* [17] and Knickerbocker *et al.* [9]. The DTA results of the three cordierite glasses were analysed primarily using the Kissinger

TABLE I Compositions of the cordierite glasses prepared for present study.

	Elements (wt %)					
Glasses	MgO	Al_2O_3	SiO_2	B_2O_3	P_2O_5	TiO_2
MAS	23.00	22.00	55.00	–	–	–
MASBP	22.00	20.00	52.00	3.00	3.00	–
MASBPT	22.00	20.00	52.00	2.00	2.00	2.00

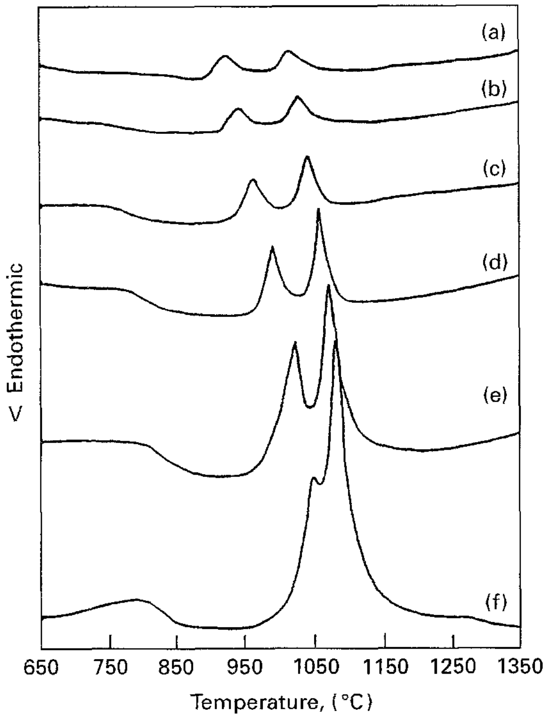

Figure 1 The differential thermal analysis (DTA) curves of the MAS glass at the heating rates of (a) 3, (b) 5, (c) 10, (d) 20, (e) 40, and (f) 80 °C per min.

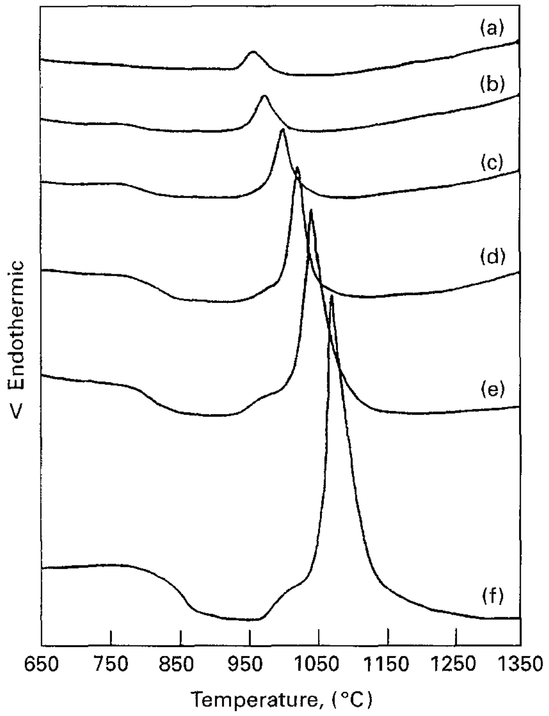

Figure 2 The differential thermal analysis (DTA) curves of the MASBP glass at the heating rates of (a) 3, (b) 5, (c) 10, (d) 20, (e) 40, and (f) 80 °C per min.

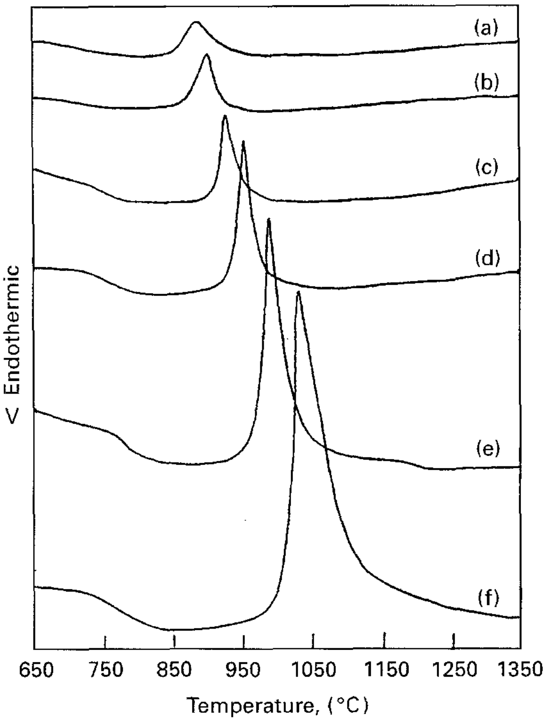

Figure 3 The differential thermal analysis (DTA) curves of the MASBPT glass at the heating rates of (a) 3, (b) 5, (c) 10, (d) 20, (e) 40, and (f) 80 °C per min.

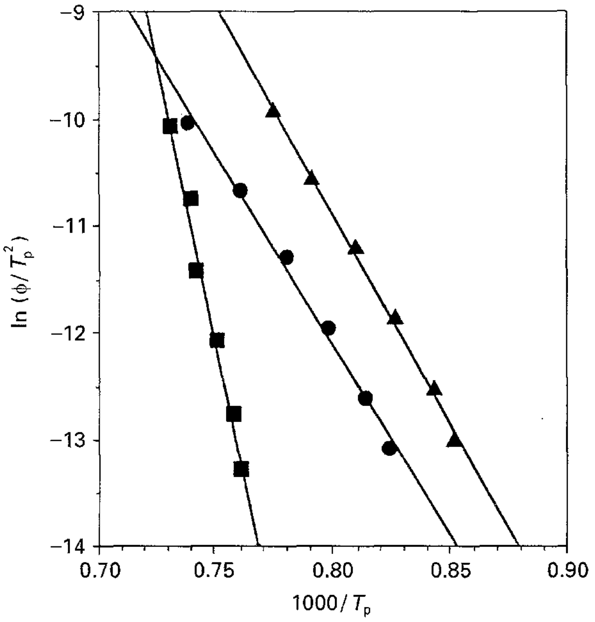

Figure 4 The Kissinger plots of the (■) MAS, (●) MASBP, and (▲) MASBPT glasses.

equation [19]:

$$\ln(\phi/T_p^2) = -E_{ck}/RT_p + \text{const.} \quad (1)$$

where ϕ is the DTA heating rate; T_p is the crystallization peak temperature; E_{ck} is the activation energy for crystallization estimated by the Kissinger method; and R is the gas constant. The Kissinger plots according to Equation 1 for the three glasses appear in Fig. 4. The MASBP and MASBPT glasses show an activation energy value of 316 and 328 kJ mol^{-1}, respectively, whereas the MAS glass has a larger activation energy value of 872 kJ mol^{-1}. Thus the formation of α-cordierite from μ-cordierite requires a much higher activation energy than that from a glass containing nuclei such as titanates. Finely distributed titanates or TiO_2-rich phases in a glass would tend to be more effective as crystallization sites compared to the grain boundaries in μ-cordierite.

Augis and Bennett [20] modified the Kissinger equation in order to allow its application to heterogeneous solid state reactions. The modified equation

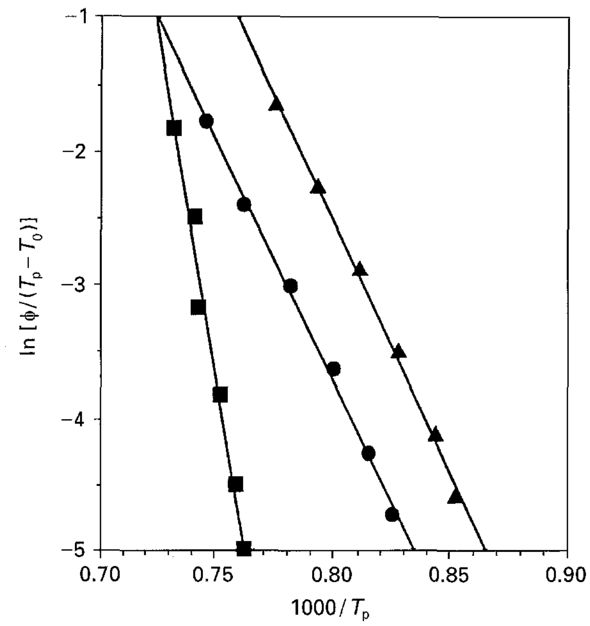

Figure 5 The Augis–Bennett plots of the (■) MAS, (●) MASBP, and (▲) MASBPT glasses.

is;

$$\ln(\phi/(T_p - T_o)) \; = \; -E_{cab}/RT_p + \text{const.} \qquad (2)$$

where E_{cab} implies the activation energy value for crystallization via the Augis–Bennett method and T_o is the temperature (600 °C) from which the DTA run started. Fig. 5 shows the Augis–Bennett plots for the three glasses. The E_{cab} values for the MAS, MASBP, and MASBPT were determined as 863, 304, and 313 kJ mol^{-1}, respectively which show good agreement with the E_{ck} values.

Matusita and Sakka [21] have pointed out that the Kissinger equation is valid only when the number of nuclei is fixed during crystal growth. If most of the nuclei are formed during the DTA run, then the activation energy values from the Kissinger equation are incorrect. They suggested a modified form of the Kissinger equation:

$$\ln(\phi^n/T_p^2) \; = \; -mE_{cmk}/RT_p + \text{const.} \qquad (3)$$

where E_{cmk} indicates the correct activation energy for crystallization via the modified Kissinger method, n is an Avrami constant, and m is the dimensionality of crystal growth. When surface crystallization dominates, $n = 1$, and when crystallization occurs dominantly in the bulk, $n = 3$. The value of m is related to n as: $m = n$ when crystallization at different heating rates occurs on a fixed number of nuclei (in other words the number of nuclei is constant during the DTA runs at different values of φ); $m = n - 1$ when nucleation occurs during the DTA runs. In addition, when surface nucleation dominates, $m = n = 1$ and Equation 3 essentially reduces to Equation 1. This means that when surface crystallization dominates, the activation energy values from the Kissinger equation (E_{ck}) will become the correct values, that is $E_{ck} = E_{cmk}$.

The values of the Avrami constant can be determined by the Ozawa equation [22]:

$$[d\ln(-\ln(1-x))/d\ln\phi]_T = -n \qquad (4)$$

where x is the volume fraction crystallized at a fixed temperature T when heated at φ. The x is the ratio of the partial area at a certain temperature to the total area of a crystallization exotherm. The Ozawa and modified Kissinger equations could only be applied to the MASBPT glass since it proved impossible to obtain an exact area for the peak representing α-cordierite formation in the MAS and MASBP glasses due to the overlapping of two peaks. Fig. 6 shows the Ozawa plot for the MASBPT glass, from which the Avrami constant, n is determined as 2. Following the work of Maurer [16], Toropov *et al.* [17], and DeVekey and Majumdar [18] it is clear that this MASBPT glass contained precursor nuclei before the DTA runs commenced and thus, the dimensionality of crystal growth, m also becomes 2. Fig. 7 shows a

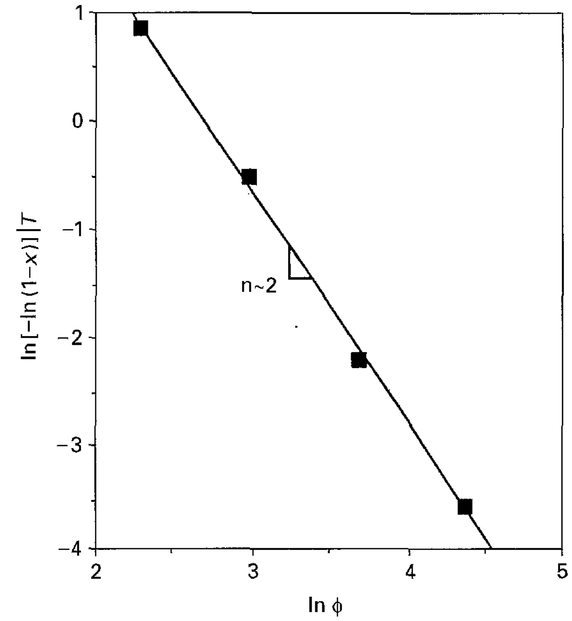

Figure 6 The Ozawa plot of the MASBPT glass.

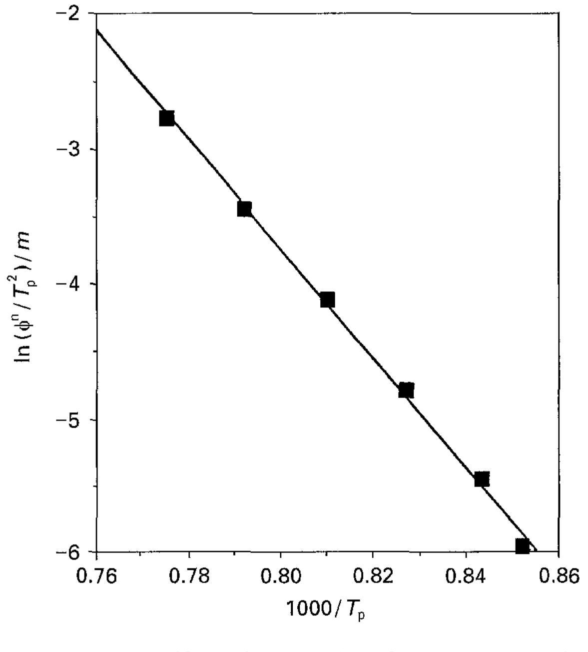

Figure 7 The modified Kissinger plot of the MASBPT glass (Avrami parameter: $n = 2$ and dimensionality of crystal growth: $m = 2$).

TABLE II Summary of DTA results of α-cordierite glasses prepared for present study.

Properties	Glasses MAS	 MASBP	 MASBPT
Avrami Parameter (n)	–	–	2
Dimensionality of Crystal Growth (m)	–	–	2
E_{ck} (kJ mol^{-1}) (Kissinger)	872	316	328
E_{cmk} (kJ mol^{-1}) (Modified Kissinger)	–	–	338
E_{cab} (kJ mol^{-1}) (Augis–Bennett)	863	304	313

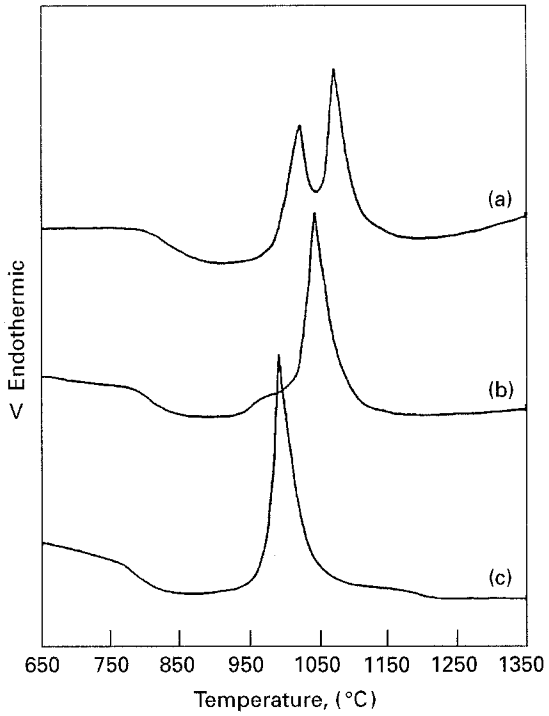

Figure 8 The differential thermal analysis (DTA) curves of the glasses of (a) MAS, (b) MASBP, and (c) MASBPT at the heating rate of 40 °C per min.

modified Kissinger plot for the MASBPT glass with $m = n = 2$, from which E_{cmk} can be determined as 338 kJ mol^{-1}. All of these DTA result are summarized in Table II.

Fig. 8 presents DTA data for the three glasses with a heating rate of 40 °C per min. The MASBP and MASBPT glasses have lower T_g (glass transition) values than the MAS glass. Due to the TiO$_2$ addition the MASBPT glass showed a 100 °C and a 50 °C lowering of T_p (crystallization peak temperature) values as compared with the MAS and MASBP glasses, respectively. In glass–ceramic systems the viscous flow of the glass above the glass transition temperature (T_g) enhances sintering. Sintering by glass flow will be hindered once crystallization is initiated. Thus, in order to obtain good sintering a glass should be sintered near but below the crystallization temperature. If a glass has a T_g and T_o (crystallization onset temperature) which are close to one another, then the glass can not be fully densified by sintering below T_o since it is highly probable that crystallization would occur before sintering is completed. Thus, only a glass–ceramic which has a large temperature interval between

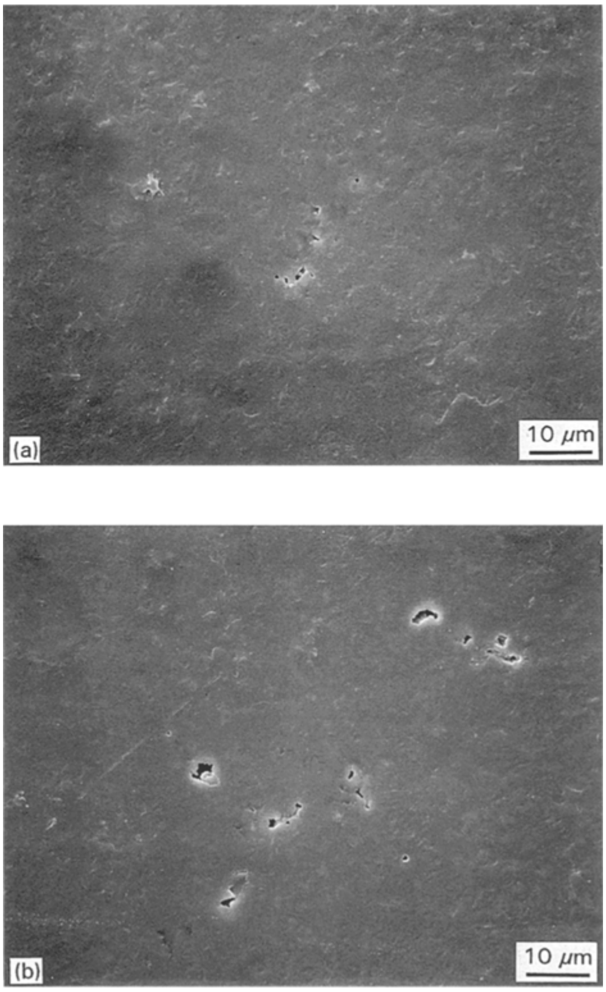

Figure 9 The scanning electron micrographs (SEM) of (a) the MASBP glass–ceramic sintered at 890 °C for 2 h and crystallized at 1050 °C for 2 h, and (b) the MASBPT glass–ceramic sintered at 850 °C for 1 h and crystallized at 1050 °C for 2 h.

TABLE III Summary of temperature values obtained from DTA results of μ-cordierite glasses prepared for present study.

Glasses	Temperature or Temperature Ranges (°C) Glass Transition (T_g)	 Crystallization Onset (T_o)	 Crystallization Peak (T_p)	 $T_o - T_g$
MAS	834	950	1078	116
MASBP	805	923	1041	118
MASBPT	770	900	989	128

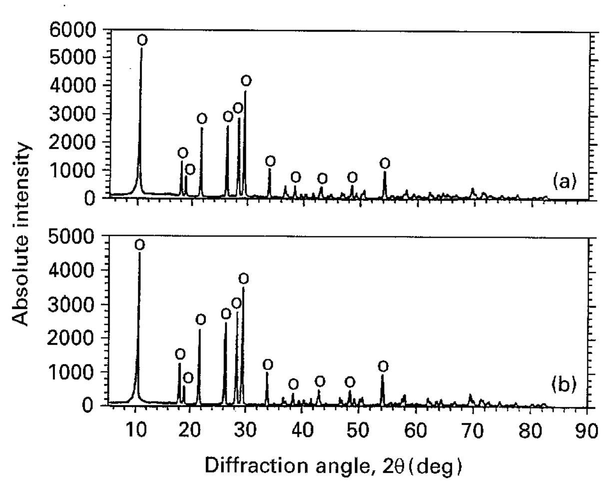

Figure 10 The X-ray diffraction (XRD) patterns showing μ-cordierite phase (○) formation in (a) the MASBP glass–ceramic sintered at 890 °C for 2 h and crystallized at 1050 °C for 2 h, and (b) the MASBPT glass–ceramic sintered at 850 °C for 1 h and crystallized at 1050 °C for 2 h.

T_g and T_o can potentially be well sintered. The T_g, T_o, T_p, and $T_o - T_g$ values for the three glasses are listed in Table III. The MASBPT glass showed the largest temperature interval of $T_o - T_g$ since it does not have an exotherm from μ-cordierite formation prior to that of α-cordierite formation. The MASBP glass also showed an increased temperature interval of $T_o - T_g$ as compared to the MAS glass. Thus, enhanced sinterability of the MASBP and MASBPT glasses is predicted. The stoichiometric MAS glass showed poor sintering as reported by Knickerbocker *et al.* [9]. Fig. 9 shows SEM photographs of (a) the MASBP glass–ceramic sintered at 890 °C for 2 h and crystallized at 1050 °C for 2 h, and (b) the MASBPT glass–ceramic sintered at 850 °C for 2 h and crystallized at 1050 °C for 2 h. Both the MASBP and MASBPT glasses showed excellent sintering behaviour. Using the Archimedes method the MASBP and MASBPT glass–ceramics showed 99.87 ± 0.08% and 99.70 ± 0.09% values of the theoretical density, respectively. The slight density difference between the MASBP and MASBPT glass–ceramics is most likely caused by a small amount of premature crystallization caused by the TiO_2 addition in the MASBPT glass. Fig. 10 shows the XRD results of (a) the MASBP glass–ceramic sintered at 890 °C for 2 h and crystallized at 1050 °C for 2 h, and (b) the MASBPT glass–ceramic sintered at 850 °C for 2 h and crystallized at 1050 °C for 2 h. Both the XRD patterns show the formation of the α-cordierite as the major phase.

4. Conclusions

(1) From DTA measurements two exotherms (one for μ-cordierite formation from a glass and the other for phase transformation from μ-cordierite to α-cordierite) were observed in the MAS and MASBP glasses, whereas only one single exotherm for α-cordierite formation was observed in the MASBPT glass.

(2) From the DTA results the activation energy values for the crystallization of α-cordierite in the MAS, MASBP, and MASBPT glasses were determined as 868 ± 5, 310 ± 6, and 326 ± 13 kJ mol^{-1}, respectively. This implies a decreased viscosity from B_2O_3 and P_2O_5 addition and also titanates or TiO_2-rich phases acting as nuclei for the α-cordierite phase formation are very effective in enhancing crystallization.

(3) From the DTA results the MASBPT glass showed a mixed (surface and bulk) crystallization mechanism (Avrami parameter: $n = 2$), which most probably results from the existence of precursor nuclei.

(4) From the DTA measurements with a heating rate of 40 °C per min T_p values for the MAS, MASBP, and MASBPT glasses were determined as 1078, 1041, and 989 °C, respectively. The T_p value for the MASBPT glass is the lowest one since it has a lower viscosity due to the B_2O_3 and P_2O_5 addition and precursor nuclei formed by the TiO_2 addition.

(5) The MASBP and MASBPT glass–ceramics showed highly dense bodies due to excellent sintering characteristics that were confirmed by SEM and Archimedes method.

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