Crystallisation of non-stoichiometric cordierite glasses

N.J. Azín, M.A. Camerucci*, A.L. Cavalieri

Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), Av. J.B. Justo 4302, Mar del Plata 7600, Argentina

Abstract

The crystallisation of a cordierite non-stoichiometric glass (25 wt.% Al_2O_3, 63 wt.% SiO_2 and 12 wt.% MgO) located in the cordierite crystallisation field in the $Al_2O_3 \cdot SiO_2 \cdot MgO$ system was studied. Glass fragments were obtained by quenching the melt in cold water. Two granulometric fractions, fine (51.8 wt.% < 37 μm) and coarse ($D_{50} = 239$ μm), were prepared by crushing, dry milling and/or sieving. A great tendency to devitrify and a high glass transition temperature ($T_g = 830$ °C) were determined. Temperatures between 940 and 1300 °C and times up to 24 h were selected in order to crystallise the glass. The crystallisation was followed by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Three exothermic peaks between 970 and 1180 °C assigned to μ- and α-cordierite crystallisations with different overlapping degrees depending on both the glass particle size and the heating rate were registered by DTA. No difference was established with respect to the crystallisation mechanism of stoichiometric cordierite glass. However, it was possible to differ the temperature of crystallisation of α-cordierite from both surface and bulk mechanisms. Three non-isothermal methods were used to estimate the activation energy to μ-cordierite crystallisation from both glass granulometric fractions.
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1. Introduction

Cordierite ($2Al_2O_3 \cdot 5SiO_2 \cdot 2MgO$) is an attractive ceramic material for use in fast cycle furnaces, among other applications [1], owing to its high thermal shock resistance due to its very low thermal expansion coefficient and its high thermal conductivity. Moreover, cordierite and cordierite based glass ceramics are promising materials as substrate to replace alumina, conventionally employed in the electronic industry [2,3], because of their low dielectric constant, high resistivity, elevated thermal and chemical stability, very low thermal expansion coefficient and modest processing costs.

The processing of cordierite based materials presents several problems [4,5]. Glassy phases generated during thermal treatments and located in both triple points and grain boundaries improve the sintering performance of these materials but deteriorate their thermal and electrical properties. However, the glassy phases could be crystallised by thermal treatment after sintering or by the incorporation of nucleating agents [6–11].

It has been shown that the crystallisation of compositions close to that of stoichiometric cordierite depends on the particle size of the glass [12,13]. Moreover, if the content of one of the oxides is changed, the crystallisation temperature ranges of μ- and α-cordierite as well as the stability ranges of both phases can be modified [14].

The aim of this paper is to study the crystallisation of a non-stoichiometric cordierite glass as a function of the treatment temperature and time, and the glass particle size.

2. Experimental

Differential thermal analyses (DTA) were performed in air at heating rates from 2 to 20 °C/min (Shimadzu DTA-50). The qualitative X-ray diffraction analysis (XRD) was done at 30 mA and 40 kV using Cu Kα radiation, Ni filter and a scan rate of 1° 2θ/min (Philips). Glass viscosity, η was assessed by heating microscopy between 1380 and

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* Corresponding author.

1460 °C on alumina substrates (Leitz microscope). Microstructures were examined on surfaces polished with an aqueous suspension of cerium oxide using a metallographic (Olympus PMG3) and a scanning electronic (Philips 505) microscopes.

A non-stoichiometric cordierite glass with 25 wt.% Al_2O_3, 63 wt.% SiO_2 and 12 wt.% MgO was prepared. This composition is that of the glass that accompanies the crystalline phases (cordierite and mullite) present in a material sintered at 1450 °C from a commercial powder of non-stoichiometric cordierite [15]. The studied glass is located in the cordierite crystallisation field in the isothermal section at 1450 °C of the $Al_2O_3 \cdot SiO_2 \cdot MgO$ system [16].

The glass was prepared from submicronic powders of corundum, α-quartz and MgO. The mixture was melted in a platinum crucible at 1600 °C, 2 h in an electric furnace and quenched in cold water. The obtained fragmented glass (monolithic glass, M) was dried in a stove. Its average diameter (D_{50} = 2762 μm) was determined by screening and two granulometric fractions were obtained. The fine fraction, F (51.8 wt.% < 37 μm; maximum diameter, D_{max} = 177 μm) was obtained by milling of M. The coarse fraction, C (between 297 and 149 μm; average diameter D_{50} = 239 μm) was obtained by grinding from a granulometric cutting between 2830 and 590 μm.

The low picnometric density, 2.51 g/cm^3 (stoichiometric cordierite glass density = 2.63–2.64 g/cm^3 [17]) can be explained by lower amounts of Al_2O_3 (network conditional forming) and MgO (network modifying) and higher amount of SiO_2 (network forming).

In the glass XRD pattern, a wide band of very low intensity appears between 10 and 30° 2θ, zone of the main diffraction peaks of μ- and α-cordierite crystalline phases (JCPDS Powder Diffraction Data Cards Nos. 14-249 and 13-293, respectively), showing clearly non-crystallinity.

Glass viscosity strongly decreases with increasing temperature as expected for glasses with a great tendency to devitrify and high glass transition temperature (T_g = 830 °C). The Vogel-Fulcher–Tamman equation: $\log \eta = 1.827273 + 121.4876/(T - 1354.545)$, $r^2 = 1$ (T = temperature, 1380–1450 °C) was used by fitting the experimental data.

The following thermal treatments were employed in order to crystallise both the glass granulometric fractions (F and C) and a glass fragment (M) of 4.8 mm:

- heating at a rate of 5 °C/min from 500 °C to temperatures of the exothermic peak maxima: 970, 1060 and 1170 °C for F (F1 treatment) and 1033 and 1180 °C for C (C1 treatment). Samples were prepared after 2 h soaking at these temperatures or without dwell time.
- heating at a rate of 5 °C/min from 500 to 1200 °C for: 3 h 30 min; 7 h; 10 h 30 min or 20 h 30 min (F2 and C2 treatments for F and C fractions, respectively).
- heating at a rate of 20; 15; 12; 10; 5 or 3 °C/min from 500 to 1200 °C for F (F3 treatment) and at 20; 15; 10; 5 or 2 °C/min from 500 to 1250 °C for C (C3 treatment).

- heating at a rate of 20 °C/min up to 500 °C and at 5 °C/min from 500 to 1250 °C without dwell time or after soaking for 1; 5 or 24 h for M (M1 treatment). The temperature was slightly greater than that corresponding to the peak height maximum of the DTA curve.
- heating at a rate of 5 °C/min from 500 to 940 °C without dwell time for M (M2 treatment). The temperature was lower than that corresponding to the onset of the DTA peak.

3. Results and discussion

3.1. Glass crystallisation

DTA curves of F and C fractions and M fragment at 5 °C/min are shown in Fig. 1. The onset of the temperature slope change of the thermogram and that corresponding to the maximum peak height were taken as the glass transition temperature (T_g) and the crystallisation temperature (T_c), respectively. T_g is high (830 °C) and remained constant in spite of the change of the glass particle size. For both F and C, one endothermic peak assigned to the nucleation and/or sintering and three exothermic peaks attributed to crystallisation were registered. The last peaks presented a different degree of overlapping depending on the glass particle size. It is worthy to note that several researchers reported just two exothermic peaks for glasses with similar composition as much as for the stoichiometric one [14,18,19]. Also three exothermic peaks were reported [20] but we are in disagreement with their assignation. By comparison with stoichiometric cordierite glasses [12,14,20,21], the crystallisation temperatures in the studied glass were higher. A clear influence of the particle size on its crystallisation behaviour was observed. A shift of the first and second exothermic
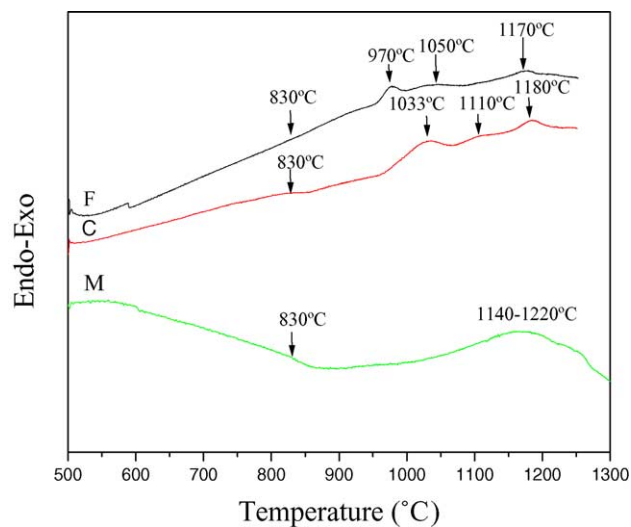

Fig. 1. DTA curves at 5 °C/min for F and C glass fractions and M monolithic glass.

peaks to higher temperatures was registered as the particle size increased, in agreement with results in the case of stoichiometric cordierite glass [12,13,21]. This fact may be associated with the occurrence of surface crystallisation. A change in this mechanism can be inferred from the insignificant shift of the third peak. For C, the exothermic peaks appear at 1033, 1110 and 1180 °C and the endothermic peak by about 970 °C. For F, the crystallisation (970, 1050 and 1170 °C) and nucleation (955 °C) temperatures resulted notably lower. On the other hand, a unique and very wide exothermic peak (∼1200 °C) was registered for M. This peak may be associated with a crystallisation directly from the amorphous material. However, it cannot discard that it is not a simple peak due to a greater overlapping.

DTA curves for F and C performed at different heating rates (F3 and C3 treatments) are shown in Fig. 2a and b. Both the overlapping of the three exothermic peaks and the crystallisation temperatures decreased by decreasing heating rates. The shift of the third exothermic peaks was very small. Facts observed at 5 °C/min were corroborated at all heating rates (Table 1). The lowest crystallisation temperatures for F and a slight shift for the third peaks for F as much as for C were registered. For F (Fig. 2a), the second exothermic peak is hard to be observed as the heating rate decreases. The three exothermic peaks of C (Fig. 2b) are wider and both the displacement of the first and second peaks at higher temperatures and their overlapping were higher. The identification of the maximum peak heights in order to determine the crystallisation temperatures turns more difficult. In short, the

higher the glass particle size and the heating rates, the higher the temperatures of crystallisation and the narrower the crystallisation temperature range.

The phase evolution determined by XRD analysis for F, C and M as a function of the thermal treatment was summarised in Table 2. Based on these results, the first exothermic peak registered by DTA was attributed to the crystallisation of μ-cordierite (970 °C for F and 1033 °C for C). The last peaks were assigned to α-cordierite crystallisation (1060 and 1170 °C for F and 1110 and 1180 °C for C). These results differ from the assignation of the second peak to μ-cordierite reported [20] for stoichiometric cordierite glass. The presence of some of the crystalline phases can be justified by the overlapping of the exothermic peaks.

Table 1
Crystallisation temperatures (T_c, °C) for the F and C glass granulometric fractions determined by DTA at different heating rates

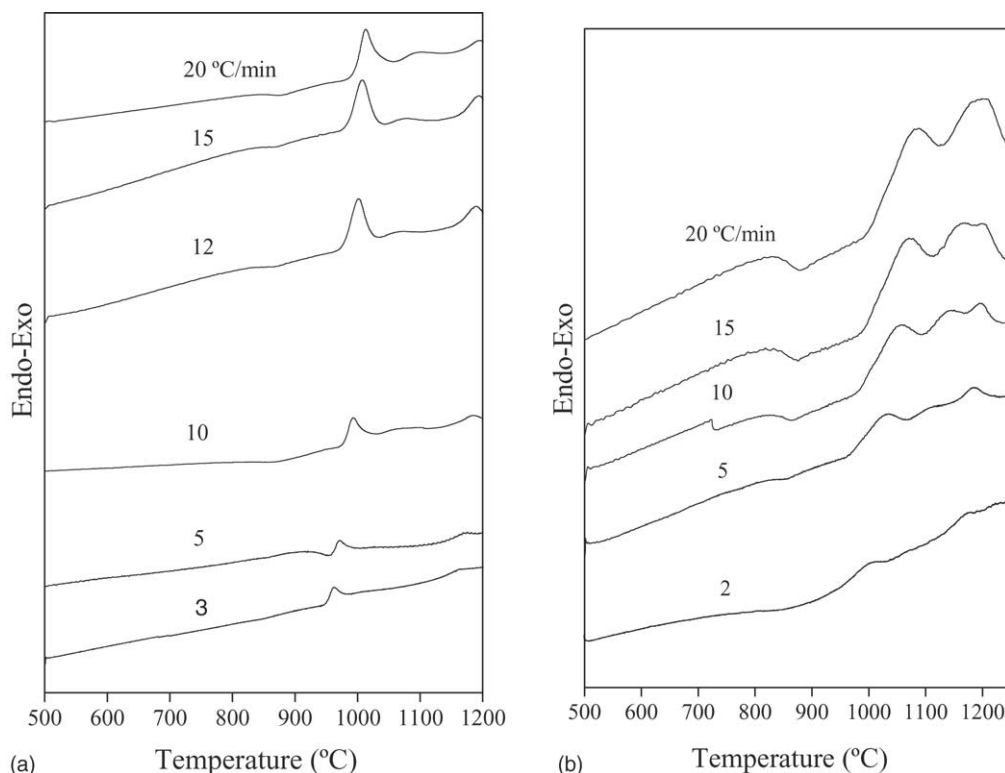| Heating rate (°C/min)	Samples					
	F			C		
	μ-cordierite	α-cordierite		μ-cordierite	α-cordierite	
2	–	–	–	1005	nd	1177
3	960	nd	1161	–	–	–
5	970	1050	1170	1033	1110	1180
10	992	1067	1183	1055	1139	1197
12	1002	1069	1189	–	–	–
15	1007	1079	1192	1069	1166	1201
20	1013	1097	1194	1085	1190	1207

nd: non determined.

Fig. 2. DTA curves obtained at several heating rates for (a) F and (b) C glass fractions.

Table 2
XRD analysis of the present phases in F, C and M samples after the different thermal treatments

Samples	Thermal treatment	Temperature (°C)	Dwell time → 0 h	Dwell time → 2 h	Dwell time → 3 h, 30 min to 20 h, 30 min
F	F1	970	Glass + μ	μ + (α)	
	F1	1060	μ + (α)	–	
	F1	1170	μ + α	α	
	F2	1200			α
	F3	1200	μ + α, for all heating rates		
C	C1	1033	μ + (α)	μ + α	
	C1	1180	μ + α	α	
	C2	1200			α
	C3	1250	α, for all heating rates		

Samples	Thermal treatment	Temperature (°C)	Dwell time → 0 h	Dwell time → 1 h	Dwell time → 5 to 24 h
M	M1	1250	glass + (μ) + α	glass + α	α
	M2	940	glass		

Phases between parentheses were determined in a little amount.

In the case of M, any crystalline phase at 940 °C was not determined. However, μ- together with α-cordierite were determined at 1250 °C. So, it could be said that the unique peak registered by DTA does not correspond to a simple crystallisation of α-cordierite directly from the amorphous supporting the proposed hypothesis of a great degree of overlapping of the three exothermic peaks. By comparison with stoichiometric cordierite glasses [12,14,20,21], μ- and α-cordierite crystallised at higher temperatures. In addition, at temperatures higher than that of the third peak, μ- and α-cordierite were confirmed by XRD indicating greater stability of μ-phase and μ- to α-cordierite transformation. A possible explanation can be given by considering that the higher stability of the μ-phase with excess of SiO_2 or with lower amounts of Al_2O_3 or MgO produce a delay in the α-cordierite crystallisation with respect to the stoichiometric glass [14]. For the studied glass composition these effects are added.

SEM images of fracture surface of F crystallised (F1 treatment) are shown in Fig. 3a and b. The glass crystallised at the temperature of the first exothermic peak (970 °C) for 2 h (Fig. 3a) exhibited principally elongated crystals with pronounced directionality which we assigned to μ-cordierite (well crystallised major phase determined by XRD) together with equiaxial small crystals. The last could be assigned to nucleus of α-cordierite (beginning of the second exothermic peak), determined as the secondary phase in the diffractogram. In the sample treated at the temperature of the third exothermic peak (1170 °C) for 2 h did not observe preferential direction of crystalline growth (Fig. 3b) and the equiaxial crystals exhibited a greater size than the nucleus observed at 970 °C. These crystals could be assigned to α-cordierite (unique phase determined by XRD). Image obtained by optical microscopy of fracture surfaces of the monolithic material crystallised at 1300 °C without dwell time at this temperature is shown in Fig. 4. Star shape

crystals immerse in the glassy bulk were appreciated. Taking into account the XRD and DTA results (Table 2), these crystals were associated with α-cordierite phase. The star shaped crystals were identified as several α-cordierite dendrites impinged on each other [21].
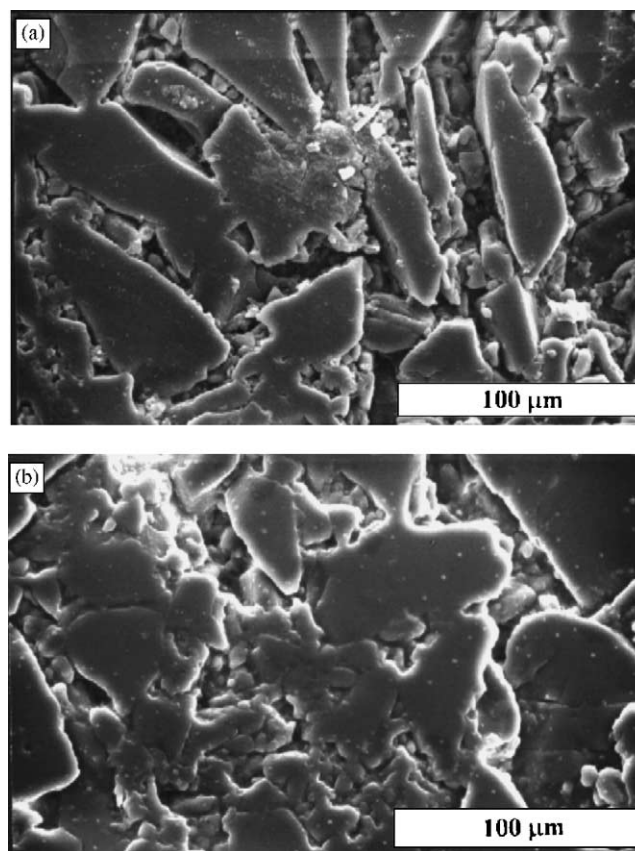

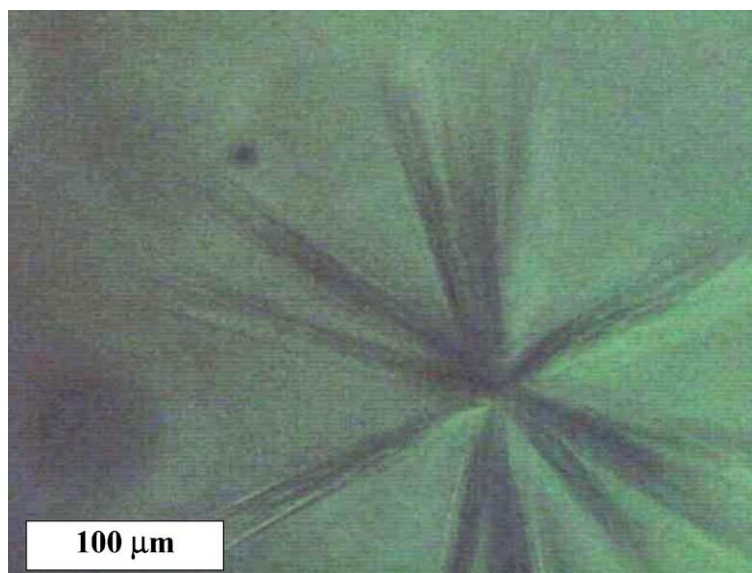Fig. 3. SEM photographs of (a) F fired at 970 °C, 2 h and (b) C treated at 1170 °C, 2 h.

Fig. 4. Optical microscopy image of fracture surface of M crystallised at 1300 °C.

3.2. Crystallisation mechanism and kinetics

A similar crystallisation mechanism to that established for stoichiometric cordierite glass [21–23] is proposed for the studied glass. This mechanism is based on the mixture of different ways of crystallisation. It is assumed that μ-cordierite crystallises directly from the amorphous (first exothermic peak) in a directional form preferentially by a surface crystallisation mechanism in agreement with other reports for cordierite glasses [12–14,21–23]. However, a distinction of both sources of α-cordierite was made. The second and the third exothermic peaks were assigned to α-cordierite crystallisation from μ-cordierite by a surface mechanism (α_1) or from the amorphous by a bulk crystallisation (α_2) [22,23], respectively. These transformations occur with different simultaneity degrees (exothermic peak overlapping) at increasing temperatures. This fact is a function of the particle size at all heating rates being α-cordierite the ultimate stable phase. By crystallising a monolithic glass (highest overlapping), α-cordierite was obtained principally from the amorphous by a bulk mechanism.

Three non-isothermal methods were employed in order to estimate the activation energy from DTA crystallisation peaks as a function of the heating rate: the modified Kissinger method [6,12], $\ln(\phi^n/T_c^2) = (-mE_c/RT_c) + C$ (T_c: crystallisation peak temperature; ϕ: heating rate; E_c: activation energy; R: gas constant; C: constant; n and m: parameters that depend on the crystallisation mechanism); the Marseglia's method [24] derived from the Kissinger one and the Ozawa method [12]. The crystallisation mechanism must be known in order to have appropriated values for n and m and it must not change with the heating rate or temperature. On the other hand, the crystallisation activation energies are compound values due to simultaneous crystallisations of the

phases (overlapping). This situation is aggravated when the mechanism changes.

For the first peak, the 'overall' activation energy can be estimated considering $n = m = 1$ for the μ-cordierite crystallisation including the beginning of the α_1-cordierite crystallisation, both by a surface mechanism [12,14]. However, for the crystallisation of the α_1- and α_2-phases it is not possible to give a unique value of n and m parameters because of a simultaneous occurrence of both surface and bulk crystallisation mechanisms. Moreover, n cannot be calculated independently from the DTA results [8] due to the difficulty in the determination of the areas under crystallisation peaks as a consequence of their overlapping. These facts did not allow us to calculate the activation energy for both crystallisations of α-cordierite.

In Fig. 5a and b, Kissinger, Marseglia and Ozawa plots for μ-cordierite crystallisation for F and C, respectively are shown. The activation energies were obtained in the ranges 439–460 kJ/mol (F) and 396–418 kJ/mol (C) depending on the method. The obtained activation energies, although somewhat higher, are in agreement with values reported for a stoichiometric cordierite glass [12] with similar particle size range and surface crystallisation mechanism. Other published data for a stoichiometric cordierite glass are comprised in a wide range ≈ 270 a 630 kJ/mol [14]. Contrarily to what would be expected for a surface crystallisation mechanism, the activation energy for F (higher amount of surface nucleation sites) resulted higher than that corresponding to C. A possible explanation for this fact is given assuming that the bulk crystallisation (α_2-crystallisation) could be operating together with the surface one at the temperatures employed in the calculus due to the higher overlapping. Therefore, the application of these methods for C is invalidated and the obtained values must not be compared with those calculated for F. These results fix a limit
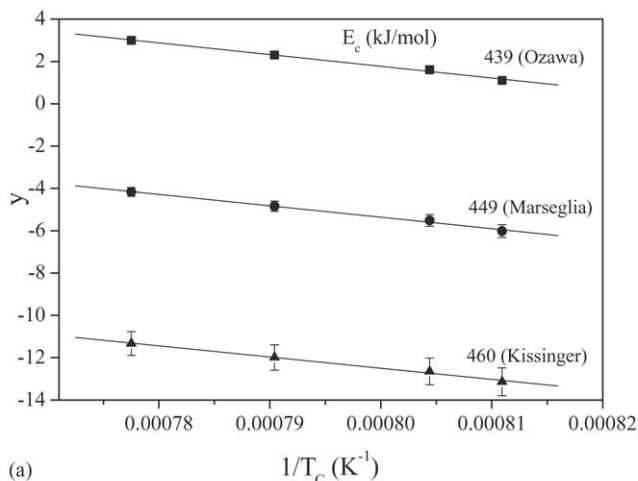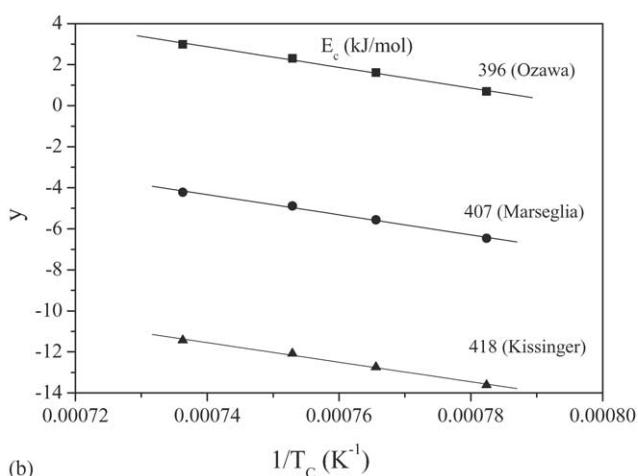
Fig. 5. Plots of y vs. $1/T_c$ (K^{-1}) $(y = \ln(\phi^n/T_c^2)$ or $\ln(\phi/T_c)$ or $\ln(\phi)$ according to Kissinger, Marseglia or Ozawa methods, respectively) for (a) F and (b) C glass fractions.

particle size to the application of these methods: at least the glass particle size must be lower than the average particle size of C ($D_{50} = 239$ μm).

4. Conclusions

By crystallising a non-stoichiometric cordierite glass both cordierite crystalline phases (μ- and α-) or one of them were obtained depending on the temperatures and times of treatment, and also depending on the heating rates. The crystallisation temperatures resulted higher than those of stoichiometric cordierite glass and a higher stability of μ-phase was determined.

A similar crystallisation mechanism to that of stoichiometric cordierite glass was assumed. However, it was possible to differ the temperature of α-cordierite crystallisation from both surface and bulk mechanisms. The mechanism is based on the mixture of a directional surface crystallisation for both the μ-cordierite crystallisation

from amorphous material and the transformation of μ-cordierite to α_1-cordierite and a non directional bulk crystallisation of α_2-cordierite from amorphous. These events occur at increasing temperatures being α-cordierite the ultimate more stable phase. The relative contribution of each type of crystallisation strongly depended on the particle size of the glass at all heating rates. The higher the glass particle size and the heating rates, the higher the temperatures of crystallisation and the narrower the crystallisation temperature range.

For fine granulometric fraction, the overall activation energy corresponding to the μ-cordierite crystallisation from amorphous material and the beginning of α_1-cordierite crystallisation from μ-phase (surface crystallisation mechanism) resulted in agreement with values reported for a stoichiometric cordierite glass. A glass particle size at least lower than 239 μm was established as a limit to the application of the three non-isothermal methods employed to estimate the activation energy.

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