Journal of the European Ceramic Society 20 (2000) 2191–2197

Microstructural evolution in sol–gel derived P_2O_5-doped cordierite powders

Sen Mei, Juan Yang, J.M.F. Ferreira *

Department of Ceramics and Glass Engineering, UIMC, University of Aveiro, 3810-193 Aveiro, Portugal

Received 5 August 1999; received in revised form 9 February 2000; accepted 14 February 2000

Abstract

The purpose of this paper is to analyse the effect of various amounts of P_2O_5 additive on the microstructural evolution of cordierite. In this research work, cordierite powders were prepared by sol–gel processing. The phase and microstructural evolution of the powders were characterised by DTA, XRD and SEM. The P_2O_5 additive was found to promote the μ-cordierite to α-cordierite transition at low concentrations, while a non-steady effect was shown for higher concentrations. The effect of P_2O_5 on the activation of cordierite can be attributed to the nucleation of P_2O_5 and the formation of mullite and xMgO-P_2O_5 based compounds ($x = 3, 2, 1$).

Keywords: Cordierite; Microstructure; P_2O_5; Powders; Sol–gel processes

1. Introduction

Cordierite and cordierite-based glass-ceramics have attracted interest in recent years because they have excellent dielectric properties (~5 at 1 MHz, with low dielectric loss). However, cordierite alone is difficult to sinter because of the narrow temperature range, within 25°C of its incongruent melting point (1445°C) and has relatively poor mechanical properties, which have prevented its widespread application.[1] Therefore, composite materials based on cordierite and glass, have been proposed as suitable candidates for microelectronics applications because they can be co-fired with copper at low temperatures (below 1000°C), and can match silicon in thermal expansion characteristics ($1\text{-}2\times10^{-6}$/K from 25 to 1000°C).[2–4]

In the conventional preparation process of cordierite powders, some nucleating agents, such as P_2O_5, B_2O_3 or TiO_2, are usually added to stoichiometric cordierite to control its crystallisation and decrease sintering temperatures.[5–8] The addition of nucleating agents also plays an important role in modifying the phase transformation of cordierite precursors. Knickerbocker et al.[9] found that even a small amount of B_2O_3 and P_2O_5 was effective in controlling the crystallisation of cordierite glasses and promoting the μ-cordierite to α-cordierite transition. Rudoph et al.[10] studied the effect of P_2O_5 on the activation energies for crystallisation of cordierite glasses. They observed apparent activation energy values in the range of 470–500 kJ/mol either in static or dynamic tests, although the polymorph formed is not referred to. Crystallisation behaviour in the non-stoichiometric compositions of the system $MgO–Al_2O_3–SiO_2$ was also studied by Amista et al.[11] They found that the nature of the excess component actually changes the stability ranges of μ-cordierite and α-cordierite. The calculated activation energies for the crystallisation of μ-cordierite and for the transformation of μ- to α-cordierite by the non-isothermal method were about 356 and 565 kJ/mol, respectively. However, there are few reports on the mechanism of the influence of P_2O_5 and B_2O_3 additives on the phase transition.

Recently, pure and crystalline cordierite powders were prepared by the sol–gel method using metal alkoxides.[12] The preparation of cordierite-based glass-ceramics in the ternary system by so-called sol–gel techniques has been extensively used.[13,14] Sol–gel processing can be used to synthesise multi-component ceramics with high chemical uniformity at lower temperatures and without any sintering aid compared with those required in conventional processes.

* Corresponding author. Fax: +351-234-425-300.
E-mail address: jmf@cv.ua.pt (J.M.F. Ferreira).

0955-2219/00/$ - see front matter
PII: S0955-2219(00)00063-7

In the present investigation, stoichiometric cordierite powders and P_2O_5-doped cordierite powders were prepared by sol–gel processing. The purpose of this research is to analyse the effect of P_2O_5 alone on the microstructural evolution and transformation of μ-cordierite to α-cordierite. The variation of the crystallisation behaviour of pure stoichiometric and P_2O_5-doped cordierite powders was also investigated.

2. Experimental procedure

2.1. Powder preparation

Cordierite and P_2O_5-doped cordierite powders were synthesised from tetraethyl orthosilicate (TEOS, Fluka Chemie AG, CH-9470, Buchs), $Al(NO_3)_3{\cdot}9H_2O$ (Merck KgaA, Germany) and $Mg(NO_3)_2{\cdot}6H_2O$ (Merck KgaA, Germany). TEOS, $Al(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved under vigorous stirring in ethanol and then hydrolysed by mixing with distilled water (molar ratio $H_2O/TEOS = 20$) catalysed with HNO_3. Orthophosphoric acid (BDH Chemicals Ltd Poole, UK) was then added in different proportions according to $P_2O_5/(P_2O_5$ + cordierite) weight ratios of 1.77, 3.47, 6.70, 9.74, 12.57 and 15.24%. These samples will hereafter be referred to as S_0–S_6, successively. The resulting gels were held at room temperature for 8 h and then were dried in an oven at 60 and 120°C for 1 day at each temperature.

2.2. Analytical methods

For XRD analysis, the as-prepared gel powders were ground and then heated at 5°C/min from room temperature up to 300°C, then at 3°C/min up to 500°C to burn out organic matter, followed by a heating rate of 10°C/min up to different desired temperatures with various holding times. The crystalline phases were identified by using an X-ray diffractometer (D/Max-C, Rigaku, Japan) scanning from 5 to 70° with a scanning speed of 3°/min. The degree of conversion from μ → α-cordierite, f, was determined by using the following equation:[15]

$$f = \frac{1}{1 + K^* \dfrac{I_{\mu(101)}}{I_{\alpha(110)}}} \quad (1)$$

where $I_{\mu(101)}$ is the integral intensity corresponding to the (101) peak for μ-cordierite and $I_{\alpha(110)}$ is the integral intensity corresponding to the (110) peak for α-cordierite, and K is a constant close to unit ($K \approx 1$).[15] The microstructure of the samples was observed by scanning electron microscopy (SEM) (Hitachi-4100, Japan). For a better comprehension of the crystallisation in this system, differential thermal analysis (DTA) (in-house constructed) was performed on the sol–gel derived powders, having average particle sizes of about 5 μ, including stoichiometric cordierite powder and the P_2O_5-doped powders. Samples were heated in air up to 1200°C at different rates of 3, 5, 10, 15, 20, 40°C/min with an alumina reference for calculating activation energies of the μ-cordierite to α-cordierite transition. Particle sizes of gel powders used for DTA measurements were determined by Coulter LS230 instrument (Coulter Electronics Limited, England). Assuming that the kinetics of the crystallisation process is described by the equation of Kissinger,[16] the activation energies are calculated via the expression:

$$\mathrm{Ln}(\phi/T_p^2) = E_{ck}/RT_p + \mathrm{const} \quad (2)$$

where ϕ is the DTA heating rate, T_p is the crystallisation peak temperature; E_{ck} is the activation energy for crystallisation estimated by the Kissinger method; and R is the gas constant.

3. Results

3.1. XRD analysis

The phase evolution of polymeric cordierite gel after heat treatment at 950, 1100 and 1300°C is listed in Table 1. For the samples heat-treated at 950°C for 2 h, strong μ-cordierite peaks together with traces of mullite and spinel phases could be observed in the stoichiometric sample S_0. With increasing P_2O_5 additive, μ-cordierite, α-cordierite, mullite, farringtonite and spinel all appear in the P_2O_5-doped samples from S_1 to S_3, whereas only μ-cordierite, mullite, magnesium pyrophosphate are present in S_4 to S_6. Therefore, one can say that a certain amount of P_2O_5 additive promotes the μ- to α-cordierite transition, while it also leads to the formation of undesired phases such as spinel and mullite.

For the samples heat-treated at 1100°C for 2 h, it was found that μ-cordierite was the main polymorph to be formed, together with traces of mullite and α-cordierite in the stoichiometric sample. However, for P_2O_5-doped samples (from S_1 to S_3), the intensity ratio $I_{\alpha(110)}/I_{\mu(101)}$ is much higher than that of the stoichiometric sample, S_0. The intensity ratio abruptly decreases for S_4 and becomes almost unity for S_5, decreasing again for S_6 to a level similar to S_4. Besides the intensity ratio, no other significant differences could be observed between the XRD results of S_0 and those of samples from S_4 to S_6, except an increasing amount of mullite appearing in the P_2O_5-doped samples.

Farringtonite ($3MgO{\cdot}P_2O_5$) is detected in the samples from S_1 to S_3 heat-treated for 2h, whereas magnesium pyrophosphate ($2MgO{\cdot}P_2O_5$) is detected in S_4–S_6. Some additional small peaks are also detected, which can be ascribed to presence of spinel phase, $MgO{\cdot}Al_2O_3$.

Table 1
Crystalline phases formed in the S series samples heat-treated at different temperatures for two different holding times

Samples	950°C/2 h	1100°C/2 h	$I_{\alpha(110)}/I_{\mu(101)}$	1100°C/4 h	$I_{\alpha(110)}/I_{\mu(101)}$	1300°C/2 h
S_0	μ[b] + M + S	μ + α + M + S[f]	0.3	μ + α + S	13.4	α[a]
S_1	μ + α + M + F[c] + S	μ + α + M + F + S	14.3	μ + α + S	39.3	α
S_2	μ + α + M + F + S	μ + α + M + F + S	12.5	μ + α + S	18.9	α
S_3	μ + α + M + F + S	μ + α + M + F + S	7.0	μ + α + M + F + S	0.8	α + M
S_4	μ + M + P[d]	μ + α + M + P	0.1	μ + M + P	0	α + M + P
S_5	μ + M[e] + P	μ + α + M + P	1.1	μ + α + M + P	0.2	α + M + P
S_6	μ + M + P	μ + α + M + P	0.1	μ + α + M + P	0.1	α + M + P

[a] α:α-cordierite.
[b] μ: μ-cordierite.
[c] F: Farringtonite ($3MgO{\cdot}P_2O_5$).
[d] P: Magnesium pyrophosphate ($2MgO{\cdot}P_2O_5$).
[e] M: Mullite ($3Al_2O_3{\cdot}2SiO_2$).
[f] S: Spinel ($MgAl_2O_4$).

With increasing heat-treatment time at 1100°C, the intensity ratio $I_{\alpha(110)}/I_{\mu(101)}$ increased at low P_2O_5 additive concentrations from S_0 to S_2, while it decreased for S_3 and S_4. The heat-treatment time did not promote significant changes in the phases present for higher P_2O_5 contents. Farringtonite is detected only in S_3.

With the temperature increased to 1300°C, μ-cordierite has been transformed into α-cordierite in all samples. Moreover, magnesium pyrophosphate is still detected at higher P_2O_5 additive concentrations from S_4 to S_6.

Due to overlapping, identified peaks were isolated by peak deconvolution and the degree of conversion from μ-cordierite to α-cordierite was calculated according to Eq. (1). The degree of conversion from μ→α-cordierite for different P_2O_5 additive concentrations in the samples heat-treated at 1100°C for 4 h is shown in Fig. 1. S_1 has a higher f value than the stoichiometric sample, S_0. This indicates that P_2O_5 additive slightly favours the transition from μ-cordierite to α-cordierite at low concentrations.

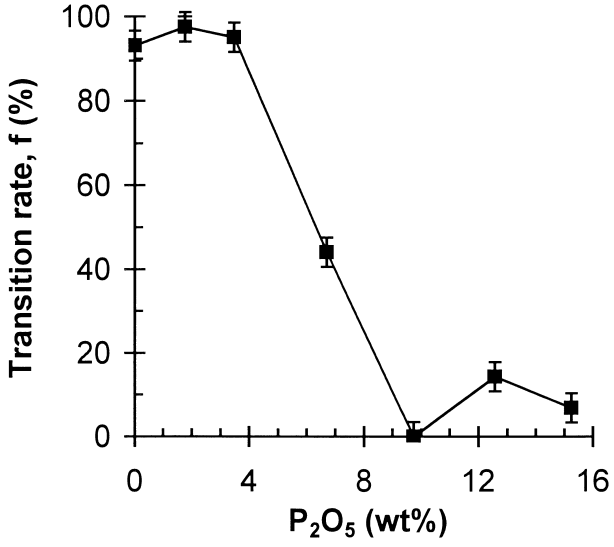

Fig. 1. The degree of conversion of S series samples heat treated at 1100°C for 4 h.

Similar f values can be observed in the samples S_0 and S_2. With the P_2O_5 additive concentrations further increasing, the degree of conversion is lower than that of S_0, although an increasing value can be observed in the sample S_5. It can be concluded that higher additive concentrations play an inhibitory role in the $MgO–Al_2O_3–SiO_2$ system.

3.2. Differential thermal analysis (DTA)

The Kissinger plots according to Eq. (2) are shown in Fig. 2. Based on these data, the calculated activation energies for the μ-cordierite to α-cordierite transition are presented in Table 2. It can be seen that the stoichiometric cordierite shows an activation energy value of 235 kJ/mol, which is about half of the values already reported for glassy cordierite powders prepared by melting.[10,11] From Table 2, it can also be noticed that the activation energy decreases for the sample containing the lowest amount of P_2O_5 additive 1.77 wt% (S_1) and then increases as the P_2O_5 additive concentration increases up to 9.74 wt% (S_4). The activation energies for the samples from S_1 to S_4 are 109, 276, 661, 701 kJ/mol, respectively. However, further additions of P_2O_5 cause a decrease of the activation energy to 303 kJ/mol for S_5, followed by an increase to 425 kJ/mol for S_6. Therefore, P_2O_5 additive promotes the μ-cordierite to α-cordierite transition up to concentrations of about 2 wt%, while a non-steady inhibitory effect is showed for higher concentrations.

3.3. Microstructural analysis by SEM

The morphology of powders heat-treated for 2 h at 950, 1100 and 1300°C is shown in Fig. 3. At 950°C there is no remarkable evidence that μ-cordierite appears in S_0 (Fig. 3a), whereas it appears in S_1 (Fig. 3b). The dendric morphology is characteristic of μ-cordierite.[17] As the concentration of P_2O_5 increases to 15.24 wt%

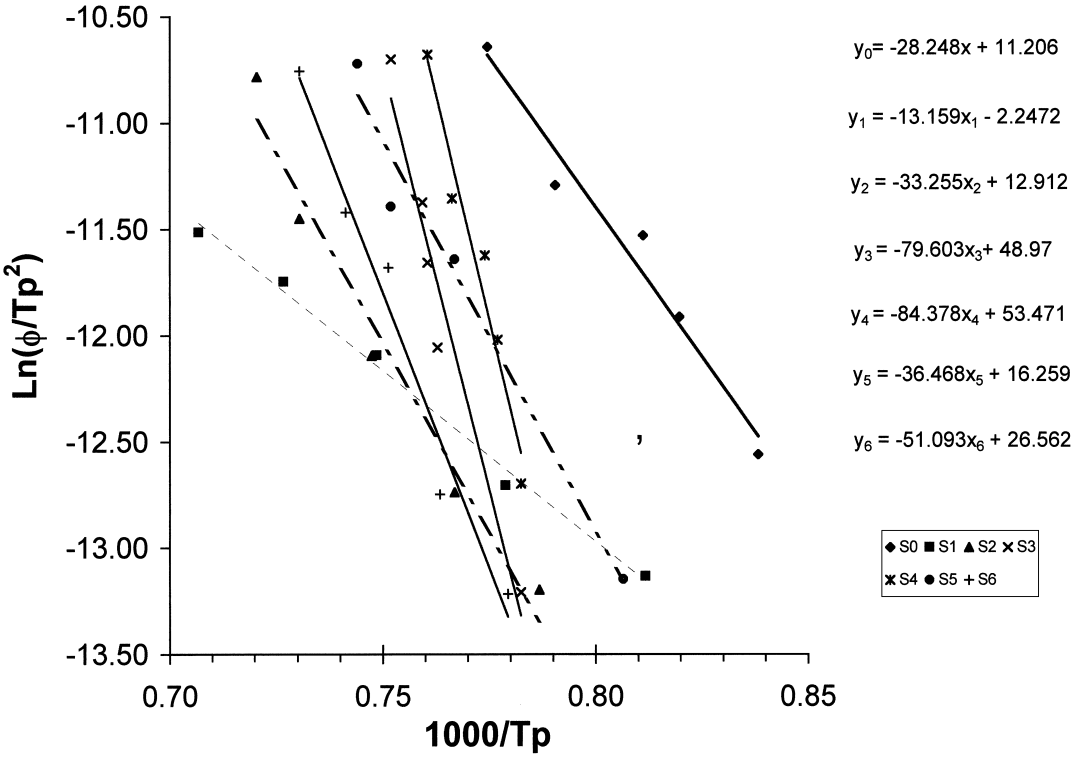

Fig. 2. The Kissinger plots for the S series samples.

Table 2
The calculated activation energies (E_{ck}) of S series samples

Sample	S_0	S_1	S_2	S_3	S_4	S_5	S_6
P_2O_5(wt%)	0.00	1.77	3.47	6.70	9.74	12.57	15.24
E_{ck} (kJ/mol)	235	109	276	661	701	303	425

(S_6), only a few μ-cordierite dendrites can be observed (Fig. 3c). Obviously, the addition of low-level of P_2O_5 favours the formation of μ-cordierite at the lower temperature, whereas higher additive concentrations delay the occurrence of μ-cordierite. After heat-treatment for 2 h at 1100°C, α-cordierite and μ-cordierite appear in S_1 simultaneously (Fig. 3d and e), particles with cellular morphology appear, which were regarded as α-cordierite.[17] This indicates that the transition μ→α-cordierite occurs at about 1100°C as confirmed by the XRD results. At 1300°C, only α-cordierite can be observed and no μ-cordierite is present in S_1 (Fig. 3f).

4. Discussion

DTA results show that the activation energy (235 kJ/mol) of μ→α-cordierite transition for the stoichiometric cordierite powders is only about half of the values already reported for glassy cordierite powders prepared by melting.[10,11] This suggests that the powders prepared by sol–gel processing should be more homogeneous than those obtained by melting, in which phase separation is likely to occur on cooling.[11] The small particle sizes of powders obtained by sol–gel method also favours the surface nucleation and crystallisation, lowering the activation energies for these processes.[18] However, the activation energies for the μ→α-cordierite transformation are strongly affected by the presence and the amount of P_2O_5 additive. Furthermore, the degree of μ→α-cordierite transformation and the microstructure of the powders also depend on the temperature and time of heat-treatment. These factors will be discussed below.

The results presented show that at lower P_2O_5 concentrations, the additive promotes the μ→α-cordierite phase transition. This is according to other earlier reports.[10,11] The promoting effect is thought to be associated with the heterogeneous nucleating role played by P_2O_5.[19] However, a radically different explanation involving immiscibility of metastable liquid has also been thought as a possible cause of very fine segregation and fine-structured crystallisation.[5] Therefore, the mechanism still remains unclear and controversial. For higher additive concentrations, the P_2O_5 starts to play an inhibitory effect and the activation energy for the μ→α-cordierite transformation increases but in a non-steady way, as shown in Table 2. Such evolution can be attributed to the formation of farringtonite at intermediate P_2O_5 concentrations (S_2 and S_3) and

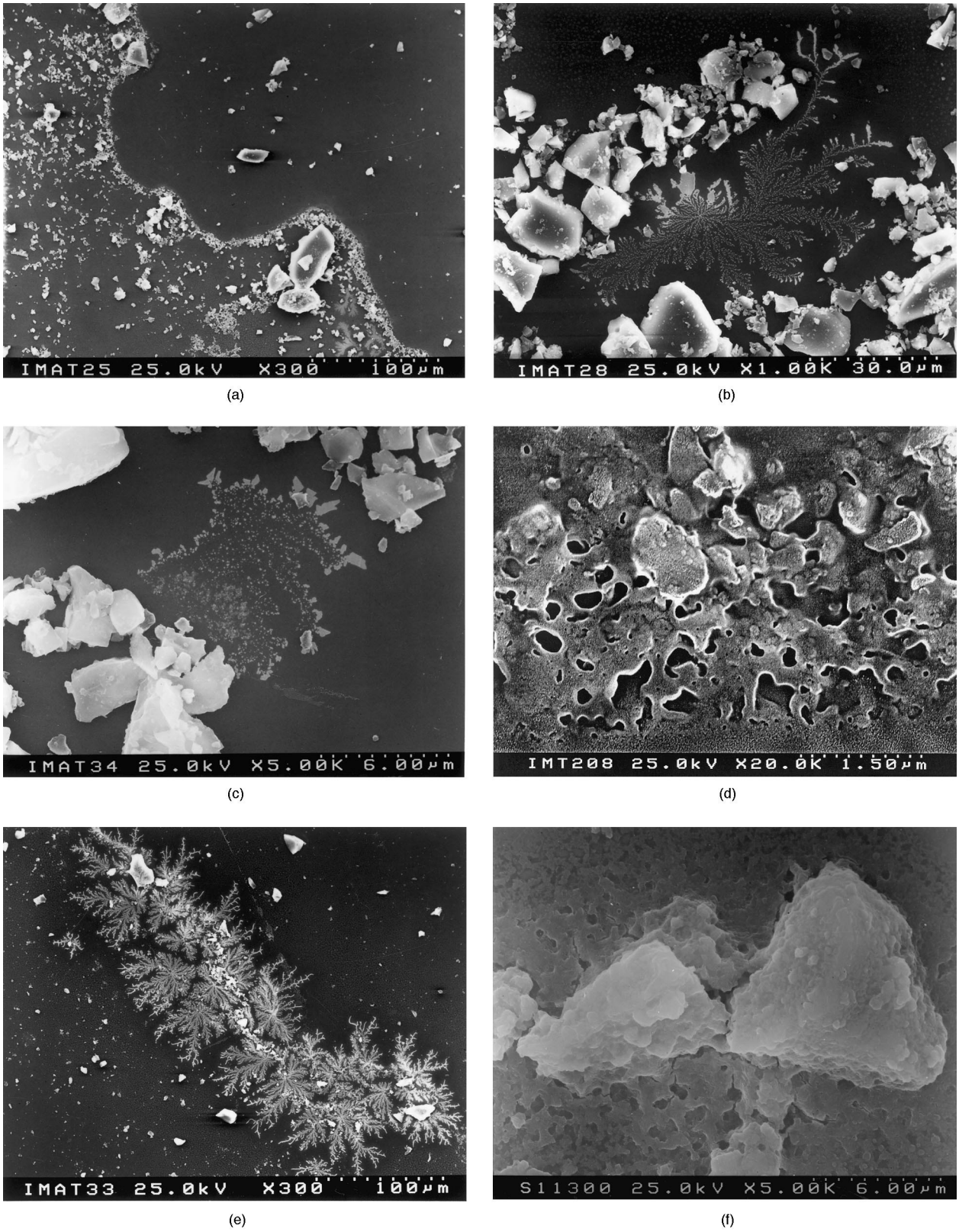

Fig. 3. The morphology of the S series heat-treated at different temperatures for different holding times (a) S_0 950°C/2 h; (b) S_1 950°C/2 h; (c) S_6 950°C/2 h; (d) S_1 1100°C/2 h; (e) S_1 1100°C/2 h; (f) S_1 1300°C/2 h.

magnesium pyrophosphate at higher concentrations (S_4 to S_6). Actually, both magnesium phosphate phases formed seem to play inhibitory roles in the μ→α-cordierite transition. The amount of farringtonite formed in the sample S_1 was too small and the promoting effect of the additive predominates. The inhibitory effect of the magnesium phosphate phases can be understood since their formation involves the consumption of MgO, driving the composition into the mullite phase field. Amista et al.[11] observed that the formation of α-cordierite is favoured near stoichiometric cordierite composition, particularly in the MgO-rich region. Therefore, competition by the P_2O_5 additive for the MgO will result in a shortage of this oxide for forming cordierite. The shortage of MgO is still somewhat aggravated due to the formation of traces of spinel phase, $MgO{\cdot}Al_2O_3$.

The complex chemical reactions occurring in the samples in the P_2O_5 additive concentrations range up to 9.74wt%, S_4, can be described as follows:

$$2MgO + 2Al_2O_3 + 5SiO_2 + xP_2O_5 \rightarrow 3MgO{\cdot}P_2O_5 + MgO{\cdot}Al_2O_3 + 2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2 + 3Al_2O_3{\cdot}2SiO_2 + SiO_2 \quad (3)$$

As the concentration of the P_2O_5 additive gradually increases from S_1 to S_3, more MgO would react with P_2O_5 to form farringtonite according to reaction (3). Therefore, cordierite was more difficult to form. This is confirmed by the increased activation energies (Table 2), observed with increasing additive concentrations. As the temperature increases to 1300°C, farringtonite reacts with mullite to form α-cordierite (Table 1).

When the concentration of P_2O_5 additive further increases from S_4 to S_6, magnesium pyrophosphate ($2MgO{\cdot}P_2O_5$) is formed at 1100°C and still persists at 1300°C. The formation of this less MgO rich magnesium phosphate is due to the gradual depletion of MgO in the composition. As a consequence, the corresponding excess amounts of silica and alumina, which initially tend to form solid solutions, will segregate as mullite phase for higher P_2O_5 concentrations. These reactions might be described as follows:

$$2MgO + 2Al_2O_3 + 5SiO_2 + yP_2O5 \rightarrow 2MgO{\cdot}P_2O_5 + 2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2 + 3Al_2O_3{\cdot}2SiO_2 + SiO_2 \quad (4)$$

The activation energy reaches a maximum at S_4 (Table 2) where magnesium pyrophosphate starts to appear. This situation should probably correspond to the higher deviation of the remaining composition from the stoichiometric cordierite composition. In fact, the intensity of the magnesium pyrophosphate peaks remains almost constant from S_4 to S_5, while those of mullite increase. The precipitation of an increasing amount of mullite would drive the remaining composition towards the stoichiometric composition. Therefore, according to the discussion above, a decrease in the activation energy might be expected, as observed in Table 2. The proportions among the cordierite forming oxides achieved at S_5 will again be changed towards the opposite direction when more P_2O_5 additive was added, S_6. This might explain why the activation energy tends to increase again.

The results show that there exists a very complicated dynamics balance between the above reactions. However, the reason that at S_5 shows a decreasing value of activation energy is uncertain. Further work is being carried out in order to clarify this point.

From the above analysis, the effect of P_2O_5 on the activation of cordierite can be attributed to the nucleating role-played by P_2O_5 and the formation of MgO-P_2O_5 compounds. At lower P_2O_5 concentrations, $3MgO{\cdot}P_2O_5$ was formed, while $2MgO{\cdot}P_2O_5$ was formed at higher P_2O_5 concentrations. It can be expected that with further addition of P_2O_5, $MgO{\cdot}P_2O_5$ will be formed.

5. Conclusions

1. The P_2O_5 additive was found to promote the μ-cordierite to α-cordierite transition at lower concentration, while a non-steady inhibitory effect was showed for higher concentrations. This effect could be attributed to the nucleating role played by P_2O_5 and to the formation of mullite and $xMgO$-P_2O_5 based compounds (x = 3, 2, 1).
2. The activation energies with various P_2O_5 additive concentrations as calculated by using Kissinger equation varied from 109 to 701 kJ/mol when the composition changed from S_1 to S_4, followed by a non-steady evolution for higher concentrations.
3. The degree of conversion from μ→α-cordierite at 1100°C with 4 h first increases with increasing P_2O_5 additive concentration up to S_1, decreasing afterwards up to zero for the sample S_4. Smaller non-steady changes are observed for higher P_2O_5 additive concentrations, which are consistent with the variations in the activation energy.

Acknowledgements

The first and the second authors are grateful to Fundação Para a Ciência e a Tecnologia of Portugal for the grants.

References

1. Byung, C. L. and Hyun, M. J., Homogeneous fabrication and densification of cordierite–zirconia composites by a mixed colloidal processing route. *J. Am. Ceram. Soc.*, 1993, **76**(6), 1482–1490.

2. Blodgett, A. J. and Barbour, D. R., Thermal conduction module, a high-performance multilayer ceramic package. *IBM J. Res. Devel*., 1982, **26**, 30–36.
3. McMillan, P. W. et al., Development of the alpha-cordierite phase in glass-ceramics for use in electronic devices. *Soc. Glass Tech*., 1985, **6**(26), 286–292.
4. MacDowell, J. F. and Beall, G. H., Low K glass-ceramics for microelectronic packaging. In *Ceramic Transactions*. Vol. 15, The American Ceramic Society, 1990, pp. 259–277.
5. Selvarj, U., Komarneni, S. and Roy, R., Seeding effects on crystallization temperature of cordierite glass powder. *J. Mater. Sci*., 1991, **26**, 3689–3692.
6. Okuyama, M., Fukui, T. C. and Sakurai, C., Phase transformation and mechanical properties of B_2O_3-doped cordierite derived from complex-alkoxide. *J. Mater. Sci*., 1993, **28**, 4465–4470.
7. Sung, Y. M., The effect of additives on the crystallization and sintering of $2MgO–2Al_2O_3–5SiO_2$ glass-ceramics. *J. Mater. Sci*., 1996, **31**, 5421–5427.
8. Sei, T., Eto, K. and Tsuchiya, T., The role of boron in low-temperature synthesis of indialite (α-$Mg_2Al_4Si_5O_{18}$) by sol–gel process. *J. Mater. Sci*., 1997, **32**, 3013–3019.
9. Knickerbocker, U., Overview of the glass-ceramic/copper substrate — a high-performance multilayer package for the 1990s. *Am. Ceram. Soc. Bull*., 1992, **71**(9), 1393–1401.
10. Rudolph, T., Pannhorst, W. and Petzow, G., Determination of activation energies for the crystallisation of a cordierite-type glass. *J. Non-Crys. Solids*, 1993, **155**, 273–281.
11. Amista, P., Cesari, M., Montenero, A., Gnappi, G. and Lan, L., Crystallisation behaviour in the system $MgO–Al_2O_3–SiO_2$. *J. Non-Crys. Solids*, 1995, **192&193**, 529–533.
12. Suzuki, H., Ota, K. and Saito, H., Preparation of cordierite ceramics from metal-alkoxides, Part 1. *Yogyo Kyokaish*, 1987, **95**(2), 163–169.
13. Ismail, M. G. M. U., Tsunatori, H. and Nakai, Z., Preparation of mullite cordierite powders by the sol–gel method: its characteristics and sintering. *J. Am. Ceram. Soc*., 1990, **73**(3), 537–543.
14. Okuyama, M., Fukui, T. and Sakurai, C., Effect of complex precursors on alkoxide-derived cordierite powder. *J. Am. Ceram. Soc*., 1992, **75**(1), 153–160.
15. Spurr, R. A. and Mysers, H., Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Anal. Chem*., 1957, **29**, 760–762.
16. Kissinger, H. E., Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand*, 1956, **57**, 217–221.
17. Glendenning, M. D. and Lee, W. E., Microstructural development on crystallising hot-pressing pellets of cordierite melt-derived glass containing B_2O_3 and P_2O_5. *J. Am. Ceram. Soc*., 1996, **79**(3), 705–713.
18. Knickerbocker, S. H., Kumar, A. H. and Herron, L. W., Cordierite glass-ceramics for multilayer ceramic packaging. *Am. Ceram. Soc. Bull*., 1992, **72**(1), 90–95.
19. Ye, R. I., Fan, Y. H. and Lu, P. W., Glass-ceramics. In *Physics Chemistry of Inorganic Materials*. China constructor industry publication, Beijing, 1984 (in Chinese), pp. 289–290.