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The effect of changing the TiO_2 content (0–6%) on the structure and thermal evolution of glasses obtained from porphyric sands and dolomite

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Abstract

Glasses have been obtained from mixtures of porphyric sands and dolomite. The influence of changes in the TiO_2 content (0–6%) on the glass structure and the formation of crystalline phases on reheating has been studied. The experimental results suggest that in the studied system TiO_2 promotes glass-in-glass phase separation and plays the role of a nucleating agent. The activation energy for crystal growth, $E_C = 486$ kJ mol^{-1}, and the Avrami parameter ($m = 1$) have been evaluated by means of thermoanalytical techniques in the case of the base glass (no TiO_2 added). The value of the Avrami parameter ($m = 1$) agrees well with SEM observations of dendritic crystal growth from surface nuclei. In the other glasses, lath-like crystals were observed, the microstructure being finer the greater the TiO_2%. The first addition of TiO_2 (2%) gives, on quenching, a partially devitrified product; subsequent additions of titania, surprisingly, allow glasses to be formed more easily. The experimental results suggest that Na_2O and K_2O, present in the porphyric sands and therefore in the glasses (to a total amount of $\approx 5.6\%$), segregate preferentially into the titania-rich phase with respect to MgO. Taking into account that Na_2O and K_2O are useful in lowering the liquidus temperature of glasses but are known to have a negative effect on the mechanical properties, this can be important in the production of glass ceramics.

Keywords: Devitrification; Silicates; Titania; Waste materials

1. Introduction

Porphyric sands produced during extraction processes represent a huge environmental problem. There is, therefore, interest in transforming them into more valuable

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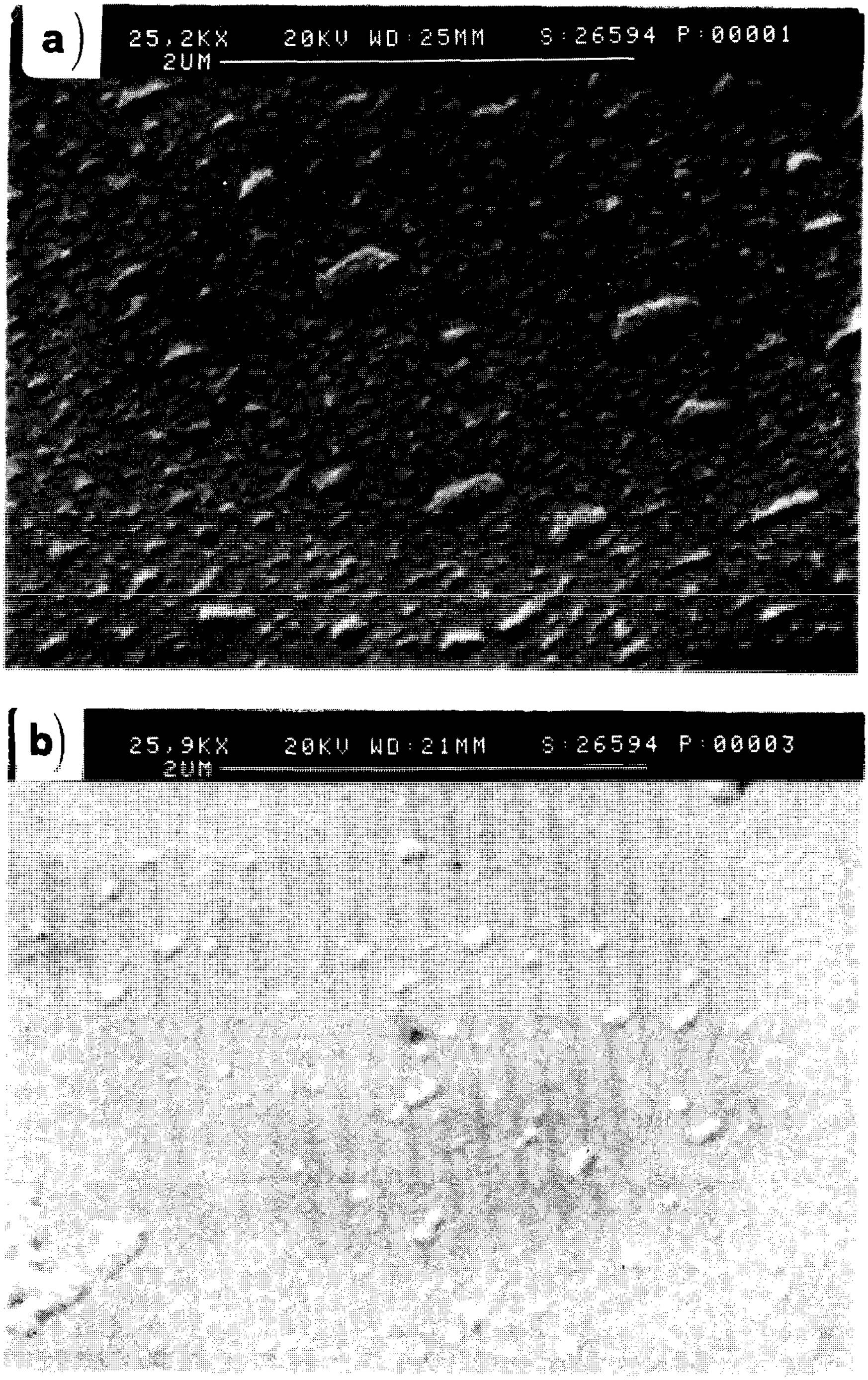

Fig. 1. SEM photographs of as-quenched samples: (a) DT-0; (b) DT-2; (c) DT-4; (d) DT-6.

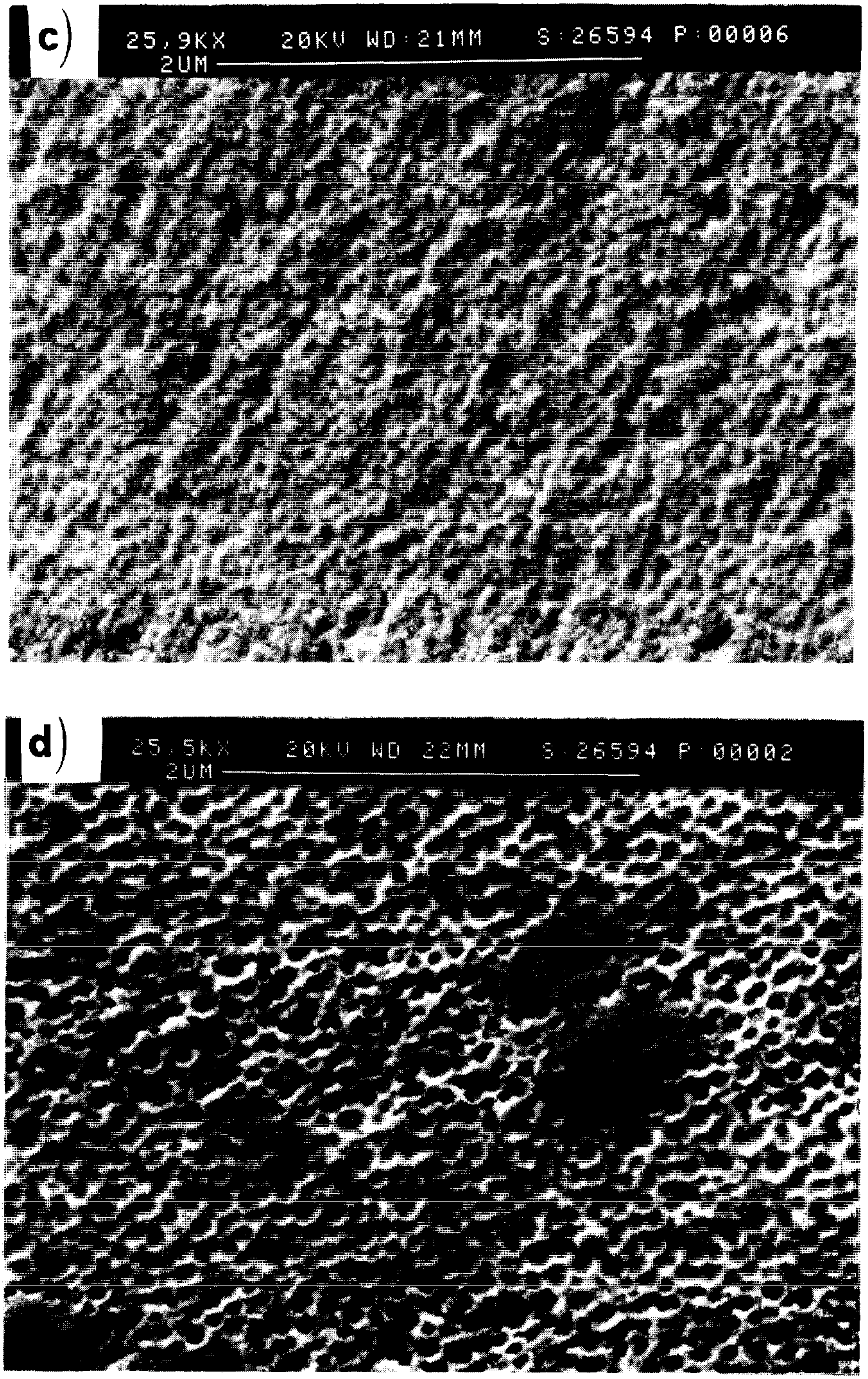

Fig. 1 *(continued)*

Table 1
Composition of porphyric sands of the studied glasses

	Porphyry	DT-0	DT-2	DT-4	DT-6
SiO_2	73.62	66.12	64.80	63.48	62.15
Al_2O_3	14.08	12.64	12.39	12.13	11.88
CaO	1.32	7.11	6.97	6.83	6.68
MgO	0.86	5.03	4.93	4.83	4.73
K_2O	4.68	4.20	4.12	4.03	3.95
Na_2O	3.05	2.74	2.68	2.63	2.58
Fe_2O_3	2.18	1.97	1.93	1.89	1.85
TiO_2	0.20	0.19	2.18	4.18	6.18

products. Porphyric sands with the compositions reported in Table 1, are crystalline materials formed of quartz, feldspar and mica. The glass ceramics in the system $CaO-MgO-Al_2O_3-SiO_2$ have interesting properties [1]; here porphyric sands have been added to dolomite, the basic component of other natural rocks, and titania has been added as a nucleating agent. This paper deals with the effect of changing the TiO_2% on the structure and thermal evolution of the glasses thus obtained.

2. Experimental

Mixtures of porphyric sand, $MgCa(CO_3)_2$ and TiO_2 were melted for 5 h at 1450°C in an electric oven. Glasses were obtained by rapidly cooling the melts to 500°C and then slowly to room temperature, to prevent cracking. The compositions are reported in Table 1. The as-quenched glasses were crushed in an agate mortar and then sieved in order to obtain $-170+230$ mesh powder particles. Differential thermal analysis (DTA) of about 90 mg of glass was carried out in static air at 10°C min^{-1} using a Netzsch differential thermal analyser (model 404M) with Al_2O_3 powder as reference material. X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) were employed to identify the crystalline phases formed and to study the microstructure developed, using Rigaku D/max IIIB and Cambridge 200 instruments respectively. The crystalline phases were identified by means of JCPDS cards [2]. Microscopical observations were performed on fracture surfaces after leaching with 3% HF solution.

3. Results

In Fig. 1, the SEM micrographs are shown relative to as-quenched samples. The DT-0 glass appears to be demixed on a very fine scale. When TiO_2 was added, a new phase is observed to form which was less resistant to acid attack and increased as TiO_2% increased.

In Fig. 2, the DTA curves are reported. The slope change in the glass transformation range is followed by a devitrification exo-peak. In the case of DT-0 and DT-2 samples, a second slope change is observed; it occurs in the temperature range of softening and is

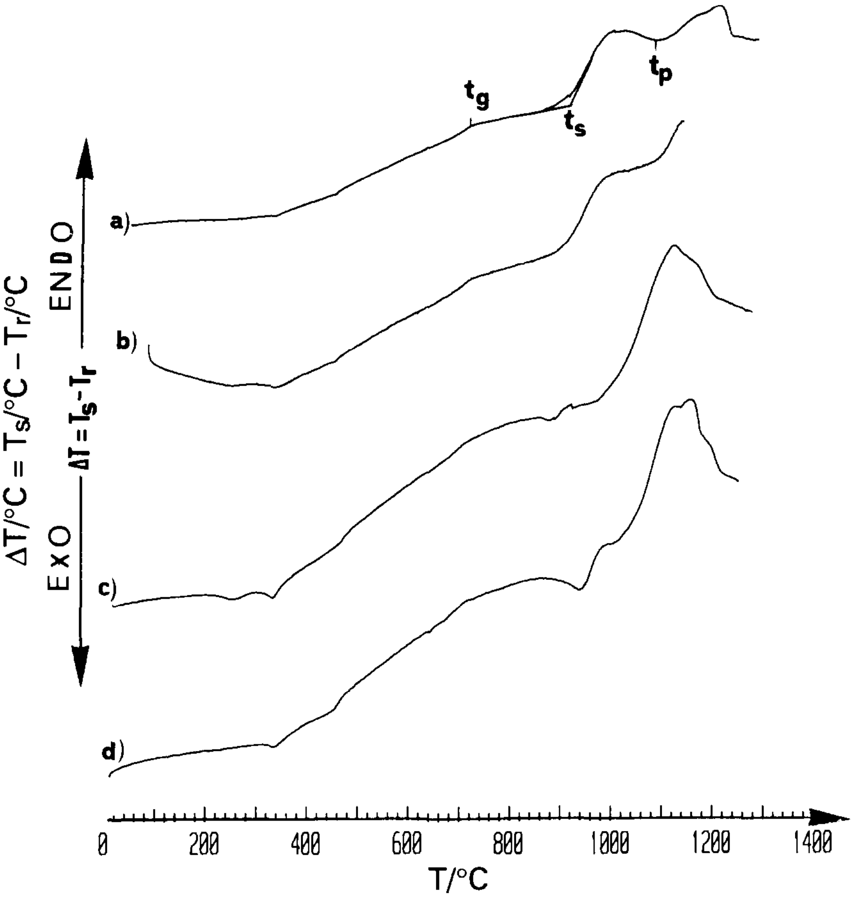

Fig. 2. DTA curves: (a) DT-0; (b) DT-2; (c) DT-4; (d) DT-6.

linked to the variation of the thermal exchange coefficient that takes place when the sample holder walls are wetted.

In Figs. 3 and 4, the X-ray diffractograms are reported for samples as-quenched and after a DTA run stopped at 1050°C. The DT-2 sample appears to be already partially devitrified after quenching. Further addition of TiO_2 gave the glasses more stability towards devitrification on quenching. When the glasses are heated above the glass transformation temperature, $CaMgSi_2O_6$ forms. It is interesting to observe that this is an inosilicate, as is the $MgSiO_3$ which forms in glasses obtained by adding only MgO to porphyric sands in the presence of TiO_2 [3]. A magnesium titanate forms when TiO_2% is sufficiently high; a similar result was obtained when no CaO was added [3]. A quantitative estimate of the crystallized percentage was obtained by evaluating the parameter [4, 5]

$$C\% = (1 - (\theta_{am}/\theta'_{am}))100$$

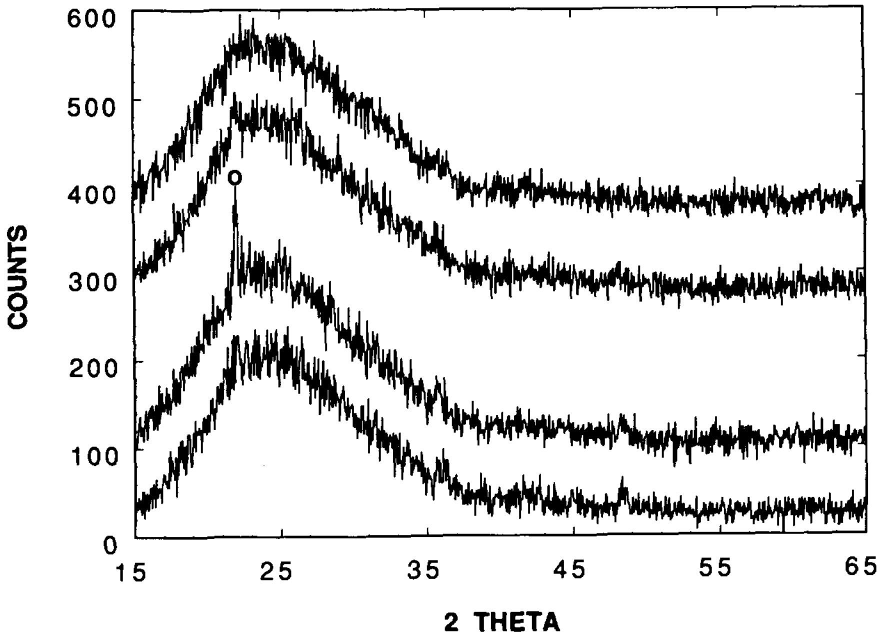

Fig. 3. XRD patterns of as-quenched samples. Sample order as in Fig. 2: ○, SiO_2 (JCPDS card 11/695).

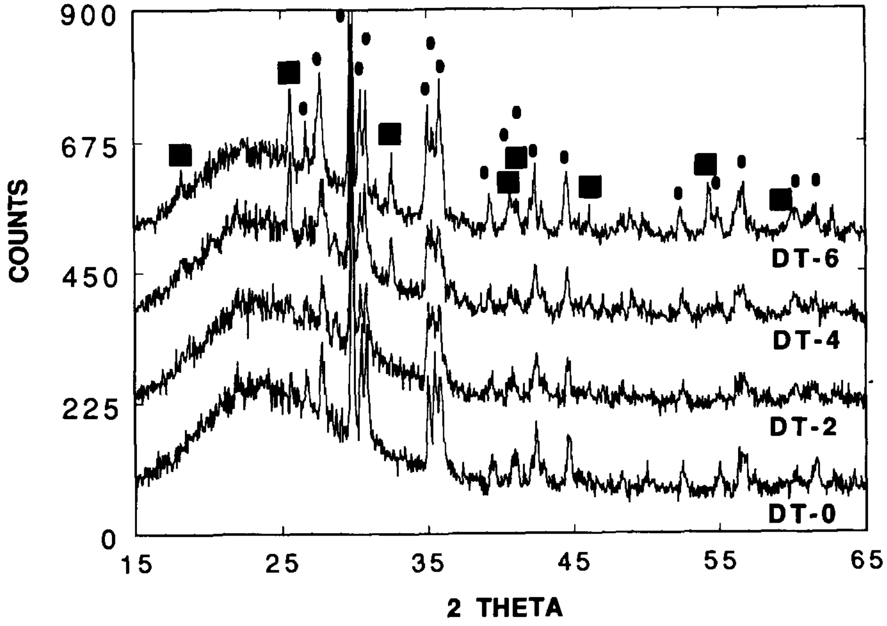

Fig. 4. XRD patterns of samples after a DTA run stopped at 1050°C. Sample order as in Fig. 2. ●, $CaMgSi_2O_6$ (JCPDS card 11/654); ■, $MgTi_2O_5$ (JCPDS card 35/792).

where θ'_{am} is the integrated intensity of the spectrum of the as-quenched samples and θ_{am} is the analogous quantity relative to the amorphous halo of the crystallized samples. In Table 2, the $C\%$ values are reported for samples heated at a constant heating rate $\beta = 10°\mathrm{C\ min}^{-1}$ till the temperature indicated.

In Fig. 5 the glass transformation t_g, softening t_S, and devitrification peak t_p, temperatures are reported, taken from the DTA curves indicated in Fig. 2. When the $\mathrm{TiO_2}$ content is increased, the difference $t_p - t_g$ decreases; this result suggests that the tendency to devitrify, on heating, increases when $\mathrm{TiO_2}\%$ is increased. This conclusion is confirmed by the observation, see Fig. 2, that only the DT-0 and DT-2 glasses devitrify after softening, i.e. when the viscosity is low enough.

Table 2
Crystallized percentages, C%, in samples heated at a constant heating rate $\beta = 10°\mathrm{C\ min}^{-1}$ to the temperatures indicated

Glass	1050°C	1150°C
DT-0	8 ± 1	21 ± 3
DT-2	19 ± 2	28 ± 3
DT-4	23 ± 3	
DT-6	32 ± 3	

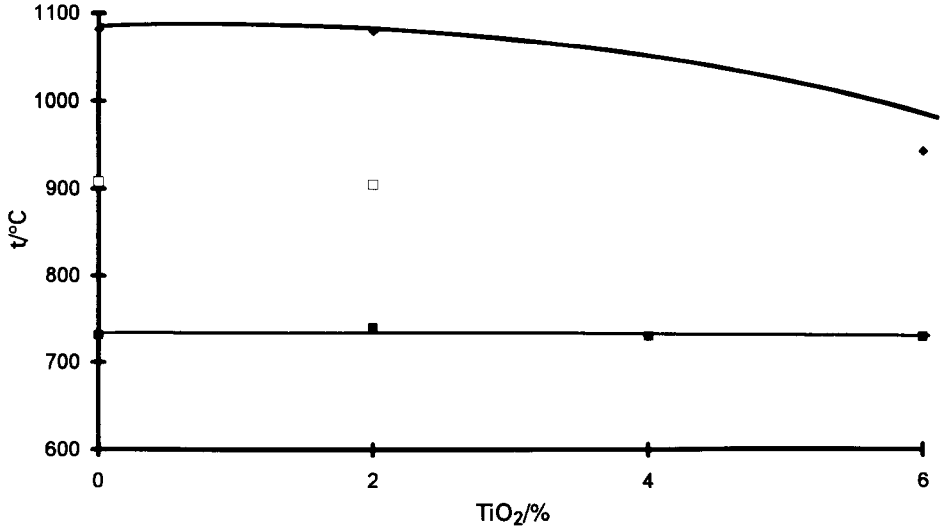

Fig. 5. Plot of glass transformation (■), softening (□), and exo-peak (◆) temperatures as a function of composition.

The non-isothermal devitrification of DT-0 glass was studied. The kinetic parameters were determined using the following two equations

$$\ln \beta = -E_C/RT_p + \text{const} \tag{1}$$

$$\ln \Delta T = -mE_C/RT + \text{const} \tag{2}$$

Eqs. (1) and (2) can be derived from the following well-known equation [6, 7].

$$-\ln(1-\alpha) = AN/\beta^m \exp(-mE_C/RT) \tag{3}$$

where α is the crystallization degree, N is the nuclei number and A is a constant; β is the heating rate, T_p the peak temperature, and ΔT_p the deflection from the base line taken as indicated in Fig. 2; T is the temperature. As in inorganic glasses, the devitrification exo-peak occurs in a temperature range higher than that of efficient nucleation [6]; E_C is the crystal growth activation energy. The parameter m depends on the mechanism

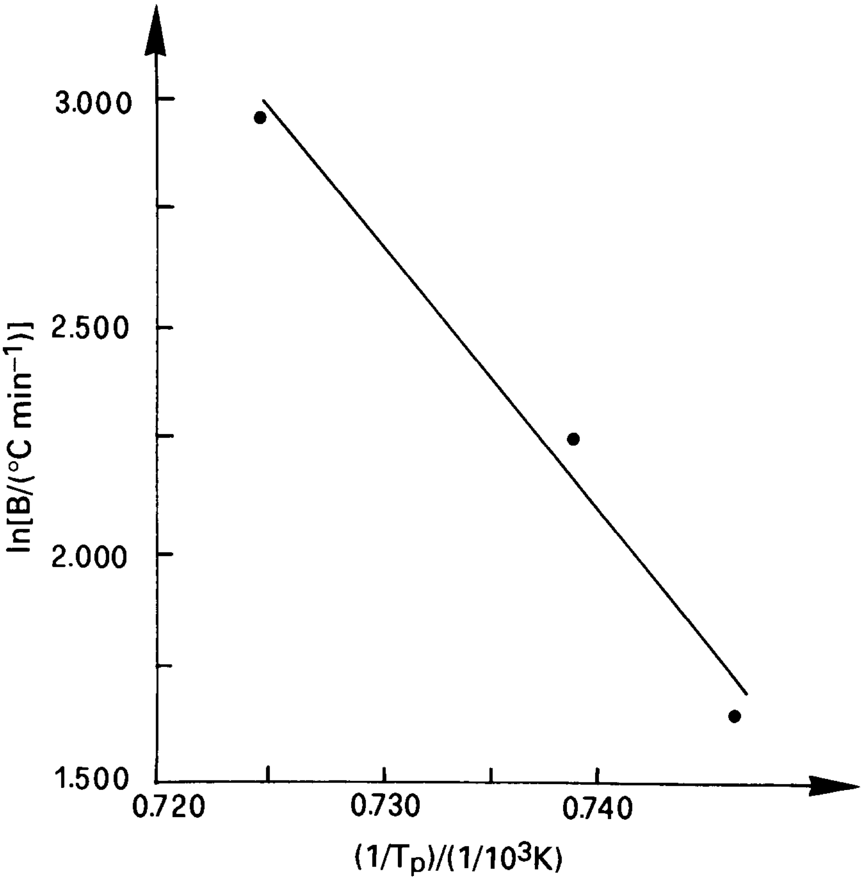

Fig. 6. Plot of ln β vs. $1/T_p$ for DT-0 glass.

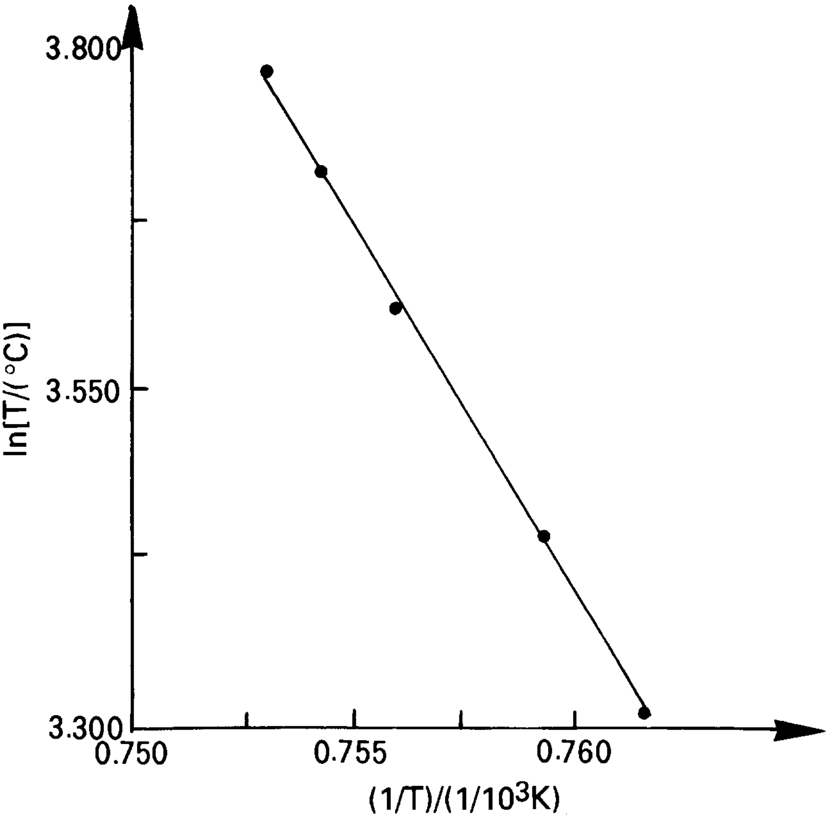

Fig. 7. Plot of ln ΔT vs. $1/T$ for DT-0 glass.

and morphology of crystal growth; it ranges from $m = 1$ for one-dimensional growth (or growth from surface nuclei) to $m = 3$ for three-dimensional growth [6, 7].

Eqs. (1) and (2) can be derived from Eq. (3) by assuming that: α at peak temperature is not dependent on the heating rate [8]; ΔT is proportional to the instantaneous reaction rate [9, 10]; and, in the initial part of the DTA crystallization peak, the change in the temperature has a much lower effect than α on ΔT [11].

In Figs. 6 and 7, the plots of ln β vs. $1/T_p$ and ln ΔT vs. $1/T$ are reported. According to Eqs. (1) and (2), straight lines are obtained. Their slopes provide the values $E_C = 486$ kJ mol^{-1} and $mE_C = 444$ kJ mol^{-1}. A value of $m \approx 1$ is, therefore, obtained. In Fig. 8, SEM photographs are reported relative to powdered samples ($<$ 230 mesh) following a DTA run stopped at 1050°C; these were taken from the DTA sample holder and represent samples that are more or less efficiently sintered. In the case of the DT-0 sample, the powder grains are still distinguishable. A dendritic crystal growth, moving from the grain surface towards the centre, is clearly observed, which agrees well with the value of $m \approx 1$ obtained. In the other cases, the samples are much better sintered: crystals in the form of laths are observed. It should be remembered that $CaMgSi_2O_6$ is

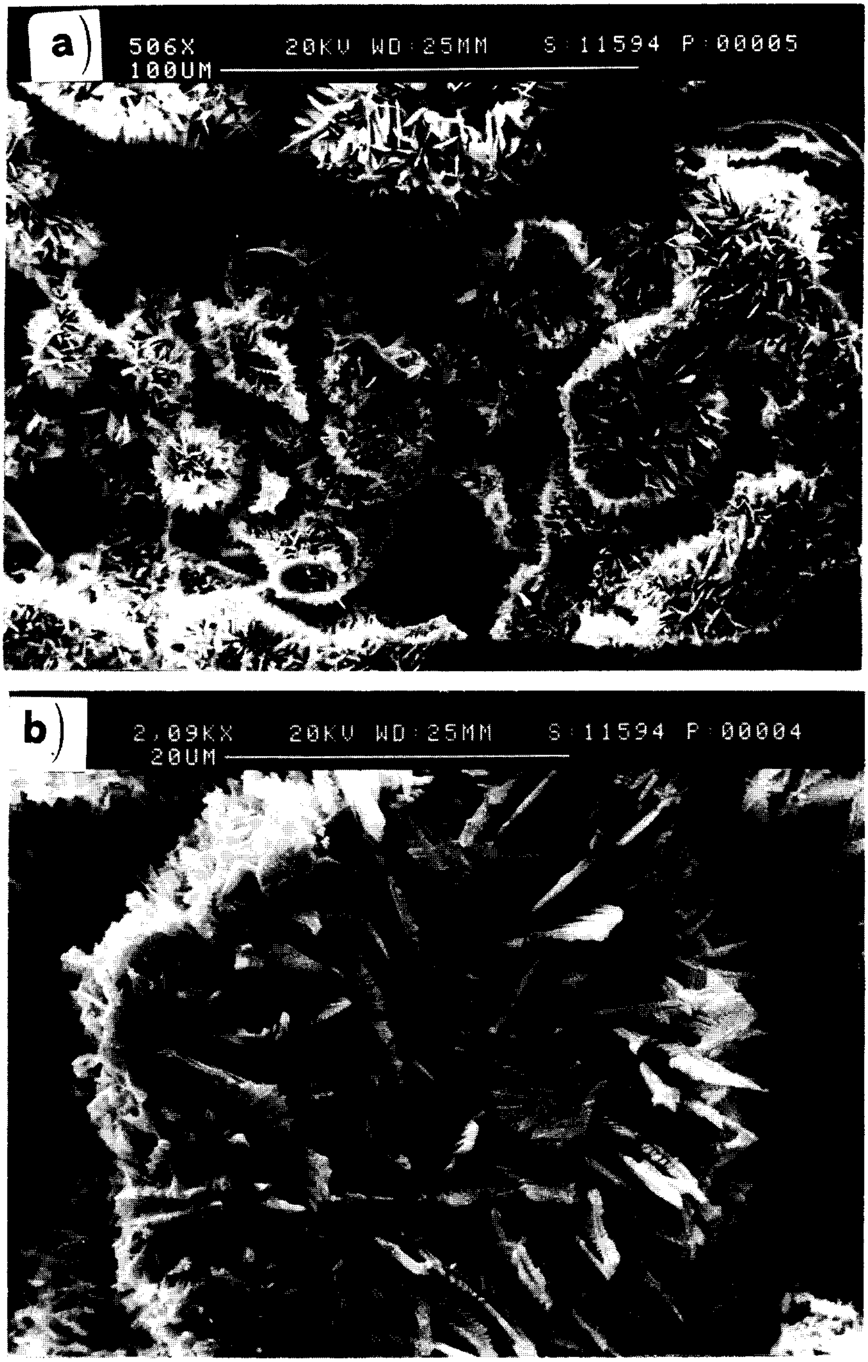

Fig. 8. SEM photographs of devitrified samples (after a DTA run stopped at 1050°C): (a) and (b) DT-0; (c) DT-2; (d) DT-4; (e) DT-6.

Fig. 8 *(continued)*

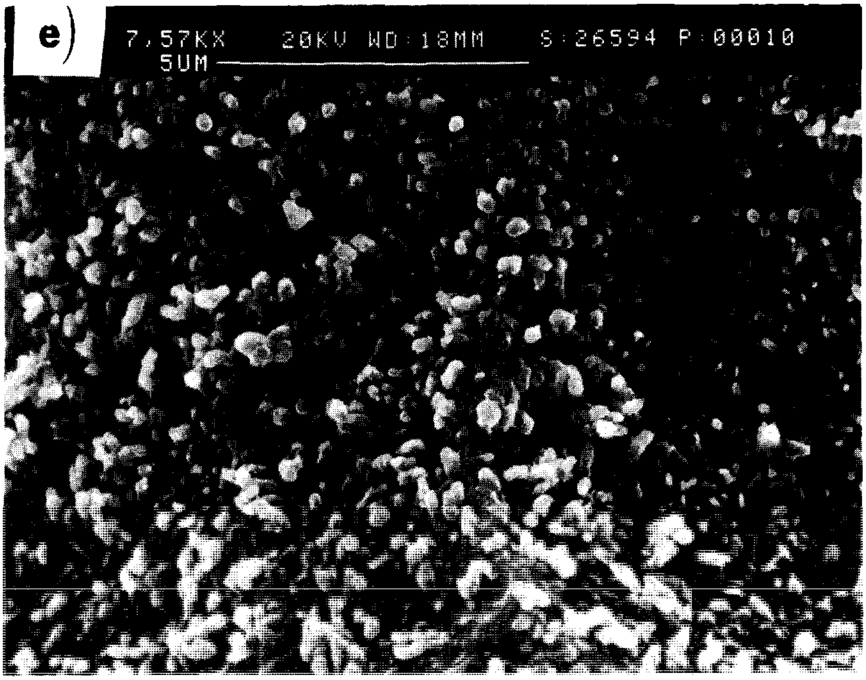

Fig. 8 *(continued)*

reported to form short prismatic crystals. The greater the TiO_2% the finer the microstructure obtained.

4. Discussion

Titanium dioxide is known to be a nucleating agent [1, 13]. De-mixing plays an important role in the controlled crystallization of titania-containing glasses [1, 13]. Although TiO_2 is soluble in a wide range of molten glasses, upon cooling and subsequent reheating, separation of a titania-rich phase is reported to occur. TiO_2 is reported to not separate out as the pure compound. In titania-nucleated $MgO–Al_2O_3–SiO_2$ glasses, magnesium titanate $MgO·TiO_2$ crystals form [13, 14]. It is also known [15] that glassy alkaline and alkaline earth silicates are demixed at high silica content. Therefore the glass in glass-phase separation observed in the DT-0 sample is consistent with this general behaviour. The photographs in Fig. 1 show that, in the studied system as well, a new glassy phase appears and increases in volume when TiO_2 is added and its amount is increased. It appears that the equilibrium between the glassy silicate phases that can be reached in the DT-0 sample changes into an equilibrium between a phase rich in silica and one rich in titania.

The increase in the tendency to devitrify, evidenced in the comment to Fig. 5, is consistent with the role of nucleating agent played by TiO_2 in silicate glasses. This is also consistent with the result that the greater the TiO_2% the finer the microstructure of the devitrified samples. If all the MgO and CaO was involved in the formation of $CaMgSi_2O_6$, a crystallized percentage $C\% = 26 \pm 1\%$ would be expected, depending on the composition. A comparison of this value with those reported in Table 2 indicates that the devitrification of DT-4 and DT-6 samples heated up to a temperature of 1050°C almost consumes the MgO and CaO content. The relatively high value found in the case of the DT-6 sample can be ascribed to the fact that in this case $MgTi_2O_5$ also forms. In the case of DT-2 and DT-0 samples, higher temperatures are needed for the devitrification. Indeed, when treated up to a temperature of 1150°C, the same X-ray diffractogram is obtained as the ones reported in Fig. 4, but the line intensities increase. The relatively low value for the DT-0 sample treated up to 1150°C could be ascribed to the observed demixing into two silicate phases. In contrast, in the case of the DT-2 sample, the entire CaO and MgO content appears to be involved in the formation of $CaMgSi_2O_6$ crystalline phase.

Two results must be pointed out. Firstly, magnesium titanate forms only at higher TiO_2 content. Secondly, the successive addition of the nucleating agent TiO_2 surprisingly inhibits devitrification on quenching, which, conversely, occurs in sample DT-2. These results are similar to those observed when TiO_2 is added in increasing amounts to glasses obtained from porphyric sands and MgO [3]. As in this case, one explanation can be found by suggesting that the alkaline oxides present in the composition of the studied glasses (in a total content of about 6.5%) segregate preferentially in the titania-rich phase with respect to MgO. As a consequence, only at higher titania content would MgO be shared between the two phases and formation of magnesium titanate be possible. The hypothesis reported may also explain the second observation. It is known that Na_2O and K_2O are classified as network-modifier oxides [13]. This means that they have a depolymerizing effect, by breaking some oxygen–silicon bonds and converting bridging oxygens into non-bridging ones. This is expected to reduce the viscosity and, thus, to enhance the tendency to devitrify. If Na_2O and K_2O segregate preferentially with TiO_2 over MgO, the first addition of TiO_2, by removing them from the silicate matrix, could well inhibit devitrification on quenching because of the consequent increase in viscosity. This is consistent with the results reported in Table 2 which indicate that in the case of the DT-2 sample, the entire amount of CaO and MgO remains in the silicate phase giving rise to $CaMgSi_2O_6$.

5. Conclusions

It is possible to obtain glass ceramics from mixtures of porphyric sands and dolomite. The experimental results suggest that in the studied system also, TiO_2 acts as a nucleating agent and promotes the glass in glass-phase separation. However, on quenching, whereas the first addition (2%) gives a partially devitrified product, successive ones allow glasses to be obtained more easily. This has been attributed to the presence of a relatively high amount (5.6%) of alkaline oxides which affects the chemical nature of the separated phases obtained upon quenching and that of the crystalline phases developed during reheating: the alkaline oxides would segregate preferentially with respect to MgO into the titania-rich phase. Because Na_2O and K_2O are useful in lowering the liquidus temperature of glasses but are known to have a negative effect on the mechanical properties, this is important in the production of glass ceramics. The activation energy for crystal growth of the DT-0 sample has been evaluated to be $E_C = 486$ kJ mol^{-1}, with an Avrami parameter of $m = 1$, which is consistent with the observation of dendritic crystal growth of surface nuclei towards the bulk of the sample.

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