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Effect of MgO content changes (8 to 15%) on the devitrification of glasses obtained from porphiric sands, MgO and TiO_2 (4%)

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Glasses have been prepared from porphiric sands, TiO_2 and $MgCO_3$ and the effect of changing the MgO content on the isothermal devitrification has been studied.

The experimental data suggest that an increase in MgO content increases the devitrification rate owing to a greater aptitude to form nuclei, so that a fine grained microstructure can be obtained more easily.

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1. Introduction

Porphiry digging produces huge sand discharges which represent a great ecological problem for soil stability. This paper is part of a work intended to convert this material, with composition, $SiO_2 = 72.40\%$, $Al_2O_3 = 13.58\%$, $K_2O = 4.60\%$, $Na_2O = 3.00\%$, $Fe_2O_3 = 2.15\%$, $CaO = 1.30\%$, $MgO = 0.84\%$, $TiO_2 = 0.20\%$, loss on calcination $= 2.06\%$, into a more valuable one. It is known that TiO_2 and MgO are useful in converting amorphous silicoaluminates into glass-ceramics [1]. In this paper the effect of changing the MgO content on the isothermal devitrification rates and the microstructure of the glass ceramics obtainable have been studied.

2. Experimental

Mixtures of the above reported composition porphiric sands, $MgCO_3$ and TiO_2 have been melted for 5 h at 1450 °C in a platinum crucible in an electric oven. The melts have been rapidly cooled to 500 °C and, then, slowly to room temperature. The glass compositions obtained are reported in Table I.

X-ray diffraction analysis (XRD) has been performed through a Rigaku D/max IIIB diffractometer equipped with a graphite curved crystal monochromator in the diffracted beam. The samples have been analysed in the $2v = 15$ to $65°$ range with a $0.02°$ step and $1° \min^{-1}$ speed using CuKα radiation. Data processing has been accomplished with a Casio 6000 computer; a search–match program, supported by JCPDS cards [2] has been used to identify the crystalline phases.

Scanning electron micrography (SEM) observations have been performed by means of a Cambridge Stereoscan-200 apparatus after etching with HF solution.

3. Results and discussion

Glass samples of the three studied compositions have been heat treated for 1 h in the temperature range 800 to 1200 °C. The X-ray diffraction patterns, relative to glasses a and c, are reported in Fig. 1. The crystalline phases formed in the glasses a and b (not reported) are the same. A slight difference is observed relative to glass c. In all cases, however, $MgSiO_3$ and TiO_2 crystalline phases have been obtained.

A quantitative estimation of the crystallized percentage has been performed by evaluating the ratio [3, 4]

$$C\% = \left(1 - \frac{Q_{am}}{Q'_{am}}\right)100$$

where Q'_{am} is the integrated intensity of the spectrum of the completely amorphous sample and Q_{am} is the analogous quantity relative to the heat-treated samples amorphous halo.

The results are reported in Fig. 3. In order to discuss them, it is worth noting that the crystallized fraction, α, dependent on the time, t, and temperature, T, can be well expressed by the Johnson–Mehl–Avrami equation [5–8]

$$\alpha = 1 - \exp(-kt^n) \qquad (1)$$

In this equation n is the Avrami parameter and depends on the devitrification mechanism and crystal morphology. The overall kinetic constant, k, is a function of the steady state nucleation, I, linear crystal

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TABLE I Composition of the studied glasses

	Glass a (wt %)	Glass b (wt %)	Glass c (wt %)
Fe_2O_3	1.94	1.88	1.78
Na_2O	2.70	2.63	2.48
K_2O	4.14	4.03	3.80
CaO	1.17	1.14	1.08
MgO	8.09	10.51	15.34
Al_2O_3	12.48	12.13	11.45
SiO_2	65.23	63.43	59.84
TiO_2	4.25	4.25	4.23

growth, U, rates and the non-steady state time lag, τ

$$k = f(IU^{n-1}, \tau) \qquad (2)$$

If the nuclei are formed before growth starts, so that their number, n^*, is constant

$$k = f'(n^*U^n) \qquad (3)$$

It is worth noting that a 2 h heat treatment at 950 °C does not change the X-ray diffraction patterns and, so, also the crystallinity percentage with respect to 1 h at the same temperature. Fig. 2 results indicate that the MgO content increase allows to obtain a glass ceramic

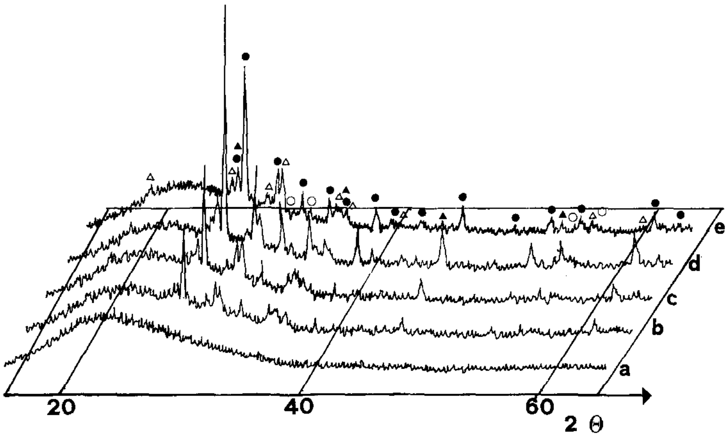

Figure 1 XRD patterns of glass a (a) quenched and after 1 h at (b) T = 850 °C, (c) T = 900 °C, (d) T = 950 °C, (e) T = 1000 °C (○) TiO_2 hexagonal (card 33-1381), ▲ TiO_2 rutile (12-1276), △ clinoenstatite (19-769), (● protoenstatite (11-273).

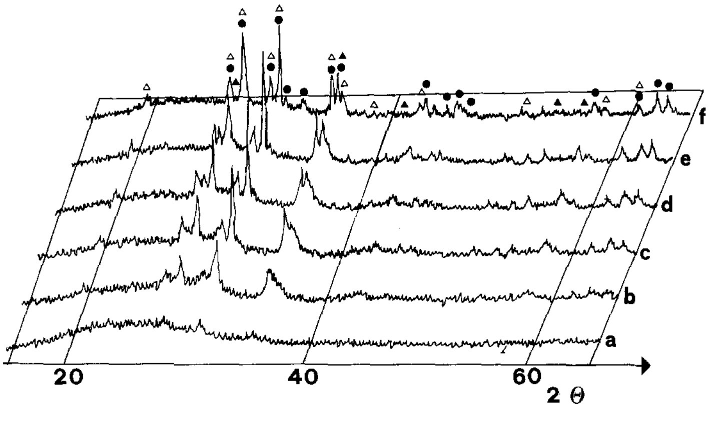

Figure 2 XRD patterns of glass c after 1 h at (a) $T = 850$ °C, (b) $T = 900$ °C, (c) $T = 950$ °C, (d) $T = 1000$ °C, (e) $T = 1100$ °C, (f) $T = 1200$ °C. △ clinoenstatite (card 19-769), ● enstatite (22-714), ▲ Rutile (21-1276)

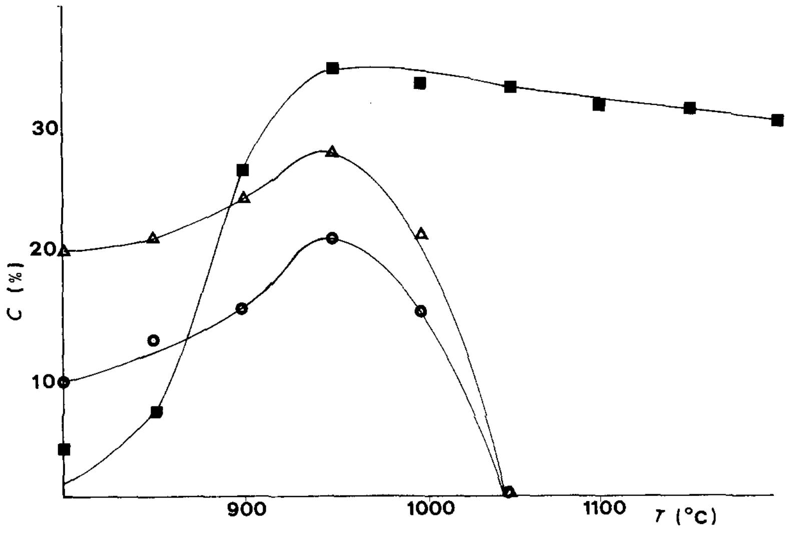

Figure 3 Crystallization degree plotted against heat treatment temperature (○ glass a, ▲ glass b, ■ glass c).

with higher crystallinity percentage. The maximum k value is at $T = 950\ ^\circ\mathrm{C}$ for glasses a and b. The location of the maximum on the glass c curve is less clear. The MgO increase causes the devitrification rates increase, but the glass c range of more efficient devitrification is shifted towards higher temperatures.

As can be inferred from Figs 1 and 2, the above reported changes of the crystallinity percentage have to be linked to the $MgSiO_3$ crystal formation kinetic.

As reported [9] for glass a and it appears in Fig. 4 for glass c, the as-quenched samples are already demixed on a very fine scale. This often occurs in glasses containing TiO_2, which is soluble in the melt but, on cooling or subsequent reheating, promotes phase separation in the form of particles rich in TiO_2.

In Fig. 5 the SEM pictures of the studied glasses after 1 h heat treatment at $T = 950\ ^\circ\mathrm{C}$ are reported. As can be seen, with increasing MgO content, a much finer microstructure is obtained. A similar result has been obtained at the other temperatures. This result suggests that the greater devitrification rates of glass c are to be ascribed to greater nucleation rates and/or a much greater preformed nuclei number in glass c. This should be linked to different phase separation behaviour, which is known [1] to determine the nucleating effect of the titanium dioxide. Taking into account relations 1, 2 and 3, the results reported in Fig. 2 suggest that, in the range 800 to 950 °C, the crystal growth rate is decreased in glass c with respect to glasses a and b.

In Fig. 6 the SEM pictures of the glass c devitrified at 1000 and 1100 °C are reported. As already found in other systems [1], the microstructural morphology is strongly dependent on the heat treatment temperature. It is known that this [1] has a great influence on the product mechanical strength, which increases as the microstructure becomes finer.

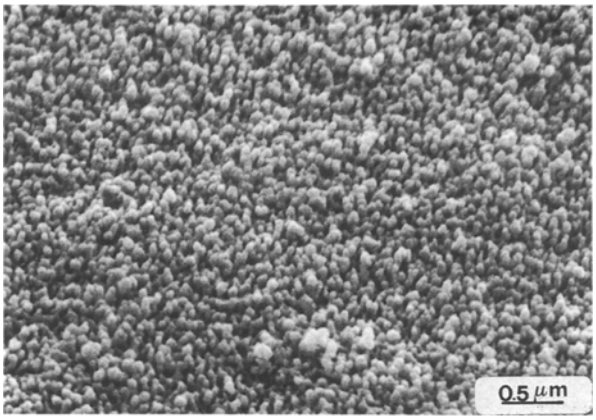

Figure 4 SEM picture of quenched glass c (3 min HF etching).

The XRD results also evidence a microstructural evolution when the heat treatment temperature is changed. It is known that for small crystallites sizes ($\lesssim 200$ nm) peak broadening occurs [10]. This effect is clearly observed, in Fig. 2, after heat treatments at temperatures lower than T = 1050 °C. A quantitative evaluation of the crystallite size was not performed because of the strong peak overlapping.

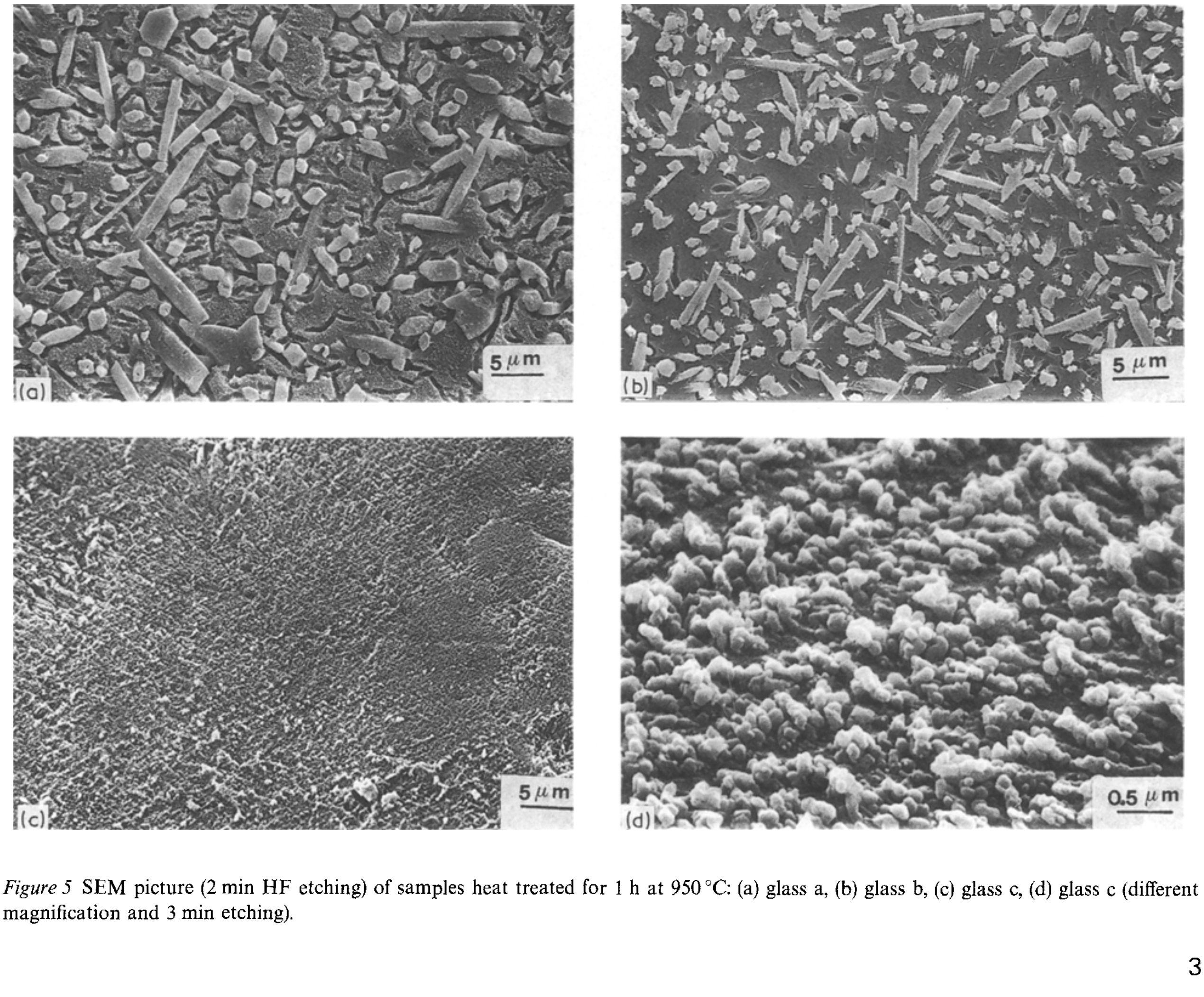

Figure 5 SEM picture (2 min HF etching) of samples heat treated for 1 h at 950 °C: (a) glass a, (b) glass b, (c) glass c, (d) glass c (different magnification and 3 min etching).

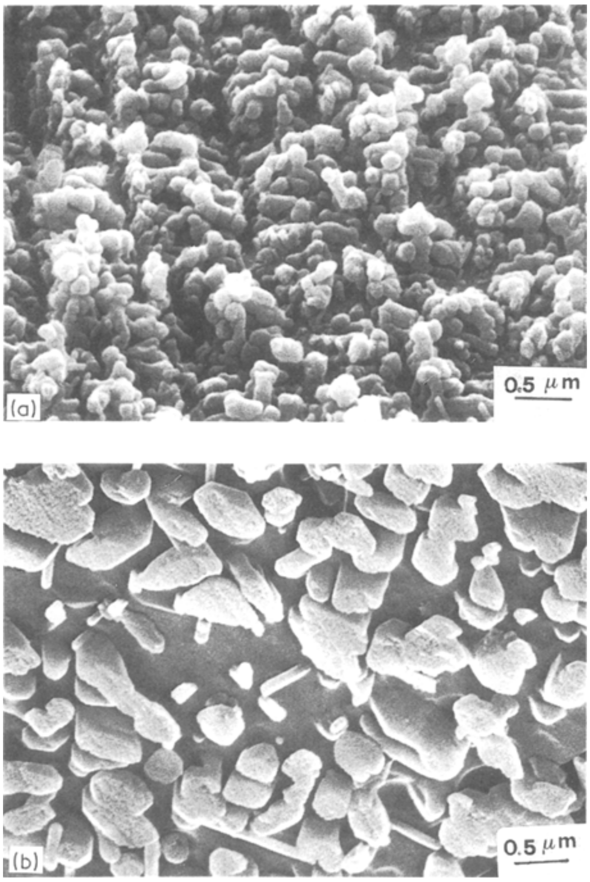

Figure 6 SEM pictures (3 min HF etching) of glass c after (a) 1 h at 1000 °C and (b) 1 h at 1100 °C.

4. Conclusions

The experimental data indicate that, in the range of the studied compositions, MgO content increases allow to obtain greater devitrification rates. This is to be ascribed to increasing aptitude to form nuclei so that more easily fine grained microstructures are obtained.

References

1. P. W. McMILLAN, "Glass Ceramics", (Academic Press, London, 1979)
2. JCPDS, International Center of Diffraction Data, 1605, Park Lane Swarthmore, Pennsylvania (USA).
3. P. H. HERMANS and A. WEIDINGER, *Macromol. Chim.* **44** (1961) 24
4. A. BENEDETTI, G. COCCO, G. FAGHERAZZI, B. LOCARDI and S. MERIANI, *J. Mater. Sci.* **18** (1983) 1039.
5. W. A. JOHNSON and R. F. MEHL, *Trans. AIME* **135** (1939) 416.
6. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
7. Z. STRNAD, "Glass Ceramic Materials", (Elsevier, Amsterdam, 1986) p. 69.
8. I. GUTZOW and D. KASHCHIEV, in "Advances in nucleation and crystallization in glasses", edited by L. L. Hench and S. W. Freiman, (American Ceramic Society, Colombus, OH, 1971), p. 116.
9. F. BRANDA, P. G. ORSINI, P. SCARDI and A. TOMASI, *Thermochim. Acta* **150** (1989) 39.
10. H. P. KLUG and L. E. ALEXANDER, "X-ray diffraction procedure," (John Wiley, New York, 1974), p. 618.

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