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DEVITRIFICATION BEHAVIOUR OF CaO–$MgO(Y_2O_3)$–SiO_2 GLASSES

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Abstract

In this paper a thermoanalytical study of the kinetic parameters and mechanism of the devitrification process of $CaO \cdot SiO_2$, $1.6CaO \cdot 0.4MgO \cdot 2SiO_2$ and $1.4CaO \cdot (0.6/3)Y_2O_3 \cdot 2SiO_2$ is reported. The experimental results suggest that, in the studied glasses, a surface nucleation process is operative; however, in finely powdered samples, that soften and efficiently sinter before devitrifying, surface nuclei behave as bulk nuclei. In this case lamellar crystalline structures are obtained.

Keywords: devitrification, glasses, kinetics, wollastonite

Introduction

In this paper the study of the non-isothermal devitrification is reported of Wollastonite ($CaO \cdot SiO_2$) and two other glasses whose composition is obtained by partially substituting CaO with MgO and Y_2O_3: $1.6CaO \cdot 0.4MgO \cdot 2SiO_2$ and $1.4CaO \cdot (0.6/3)Y_2O_3 \cdot 2SiO_2$. Scanning electron microscopy (SEM) observation has been coupled to differential thermal analysis (DTA) in order to have a better insight into the devitrification mechanism of these glasses.

It's worth remembering that CaO and SiO_2 in a molar ratio $CaO/SiO_2 = 1$ are the basic components of bioactive glasses and glass-ceramics [1, 2]. However the non-isothermal devitrification of the reported glasses appears to be interesting because during the heating cycle in a DTA apparatus, powder sintering occurs in the temperature range of efficient devitrification. As will be shown, this has relevant consequences on the devitrification mechanism.

Experimental

The glasses of composition $CaO \cdot SiO_2$, $1.6CaO \cdot 0.4MgO \cdot 2SiO_2$ and $1.4CaO \cdot (0.6/3)Y_2O_3 \cdot 2SiO_2$ were prepared by melting analytical grade reagents,

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$MgCO_3$, $CaCO_3$ and SiO_2 in a platinum crucible in an electric oven for 4 h, in the temperature range 1400–1600°C. The melts were quenched by plunging the bottom of the crucible into cold water. Thermal analysis was carried out by means of a Netzsch Differential Scanning Calorimeter (DSC) model 404M on about 50 mg powdered samples at various heating rates (2–20 $deg\cdot min^{-1}$). Fine (63–90 μm) coarse (500–315 μm) powdered samples were used. Powdered Al_2O_3 was used as reference material.

Devitrified samples were analyzed in a computer-interfaced X-ray (CuK_α) powder diffractometer (XRD) using a Philips Diffractometer model PW1710, with a scan speed of $1^\circ min^{-1}$ using a built-in computer search program. The crystalline phases were identified by means of JCPDS cards.

SEM observations were performed using a Cambridge Stereoscan 200 apparatus after 6 min of etching with 5% HF solution.

Results and discussion

In Fig. 1 the DTA curves of the $CaO\cdot SiO_2$ glass are reported recorded at 10 $deg\cdot min^{-1}$ heating rate, relative to fine (63–90 μm) and coarse (315–500 μm) powdered samples; they are representative of all the other glasses ones. When a glass is heated in a DTA apparatus a slope change appears on the recorded curve when passing through the glass transformation temperature range. As can be seen the first slope change in the glass transformation range can be followed by a second one at a temperature lower than the onset of the devitrification exo-peak. As a matter of fact in this case the initially powdered sample was recovered from the DTA sample holder as a porous body. Therefore the second slope change is to be linked to the change in the thermal exchange coefficients when powders soften and sinter. The effect is always much more pronounced in the case of the fine powders.

X-ray diffraction (XRD) analysis was performed on samples submitted to a DTA run stopped just after the exo-peak. In Fig. 1 the X-ray patterns are reported. As can be seen in the case of the Y_2O_3 substituted glass some lines could not be attributed.

The devitrification kinetic parameters were determined by using the following two equations:

$$\ln\beta = -E_c/RT_P + \text{const} \tag{1}$$

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

Equations (1) and (2) can be derived from the well known following one [3, 4].

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

were α is the crystallization degree, N is the nuclei number and A is a constant. β is the heating rate, ΔT and T_p the deflection from the base line and the peak temperature 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 [3], E_c is the crystal growth activation energy. The parameter m depends on the mechanism and morphology of crystal growth; it ranges from $m = 1$ for 1-dimensional growth (or growth from surface nuclei) to $m = 3$ for 3-dimensional growth [3, 4].

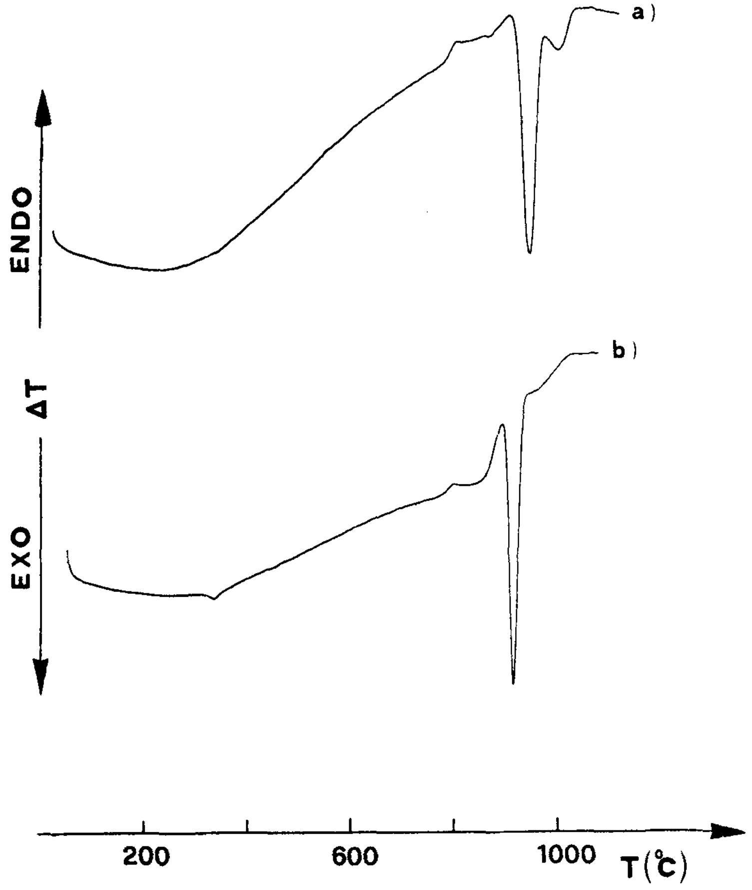

Fig. 1 DTA curves of coarsely (a) and finely (b) powdered samples of CaO·SiO$_2$ glass (β = 10 deg·min^{-1})

Equations (1) and (2) can be derived from it by supposing:

1) α at peak temperature is not dependent on the heating rate [5];

2) ΔT is proportional to the instantaneous reaction rate [6, 7];

3) in the initial part of the DTA crystallization peak the change in the temperature has a much lower effect than α on the ΔT [8].

When plotting $\ln\beta$ *vs.* $1/T_p$ and $\ln\Delta T$ *vs.* $1/T$ straight lines were obtained according to Eqs (1) and (2) (Figs 3, 4, 5). Their slopes allowed, therefore, to evaluate the E_c and mE_c values reported in Table 1. When comparing the values of E_c with the mE_c relative to fine powdered samples, values of $m \approx 2$ are obtained. On the contrary in the case of coarse powdered samples values $1 < m < 2$ were obtained. It's interesting pointing out that the mE_c values appear to increase as the specific surface of the samples is increased. Usually the opposite result is obtained [9] owing to the fact that the greater the specific surface the greater is the tendency to devitrify by growth from surface nuclei so that m is

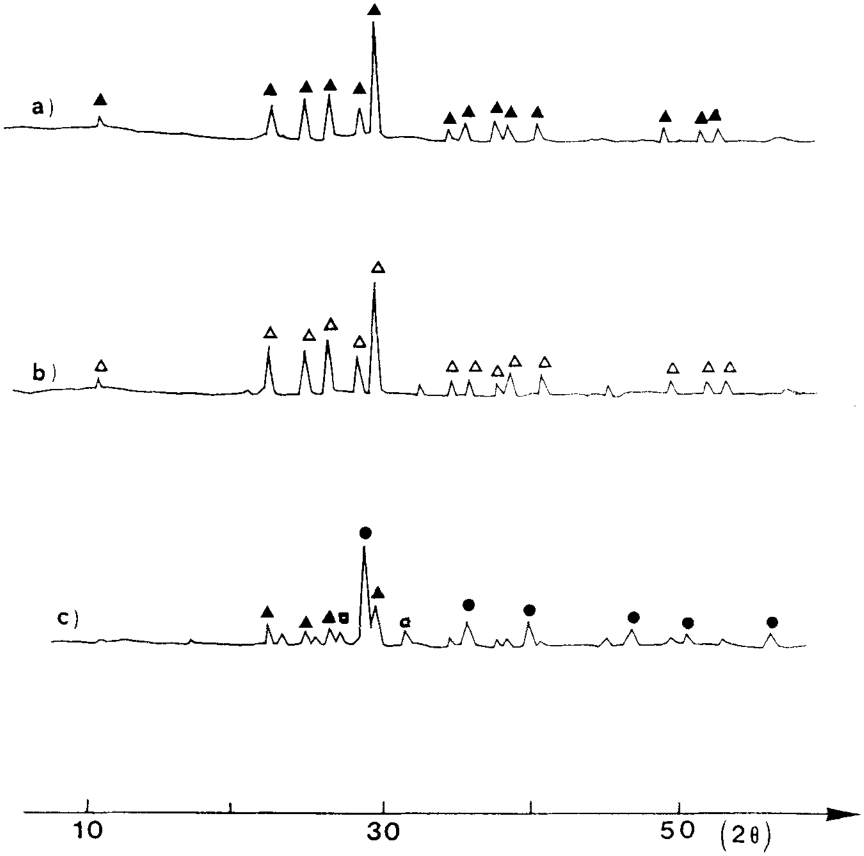

Fig. 2 X-ray diffraction patterns (after DTA run) of $CaO \cdot SiO_2$ (a), $1.6CaO \cdot 0.4MgO \cdot 2SiO_2$ (b) and $1.4CaO \cdot (0.6/3)Y_2O_3 \cdot 2SiO_2$ (c): ▲) wollastonite (JCPDS card 29/372); △) wollastonite solid solution; •) pseudowollastonite (JCPDS card 19/248); □) unknown phase

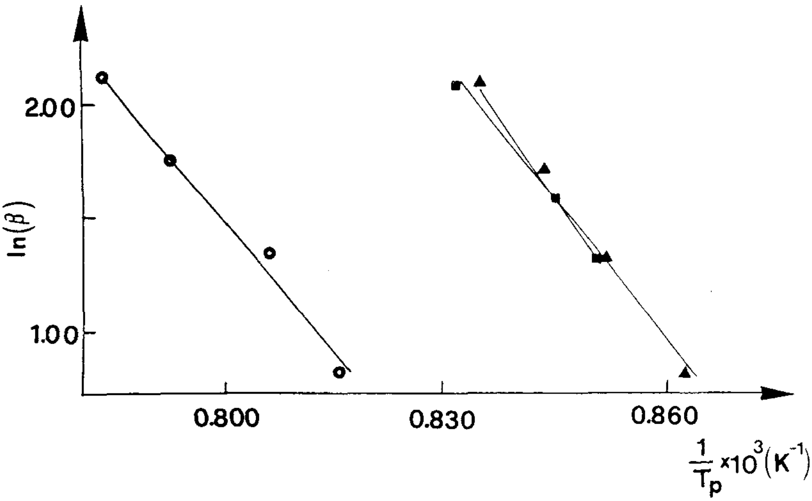

Fig. 3 Plot of lnβ *vs.* $1/T_p$: ■) $CaO{\cdot}SiO_2$; ▲) $1.6CaO{\cdot}0.4MgO{\cdot}2SiO_2$; o)$1.4CaO{\cdot}(0.6/3)Y_2O_3{\cdot}2SiO_2$

progressively reduced to the value $m = 1$. One explanation can be that devitrification, in these glasses, preferentially occurs by a surface nucleation mechanism. However surface nuclei formed in the glass transformation range can behave as bulk nuclei in powdered samples that sinter before devitrifying. As sintering is more efficient the finer are the powders, lower values of mE_c are expected in the case of coarser powders.

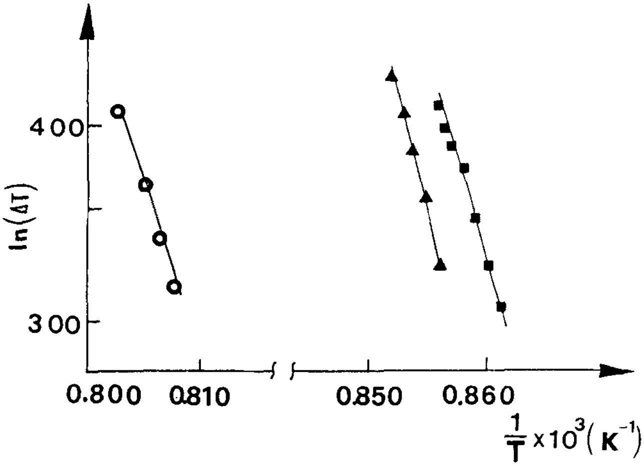

Fig. 4 Plot of lnΔ*T* *vs.* 1/*T* relative to fine powdered samples (63–90 μm) (symbols as in Fig. 3)

It's useful observing that the value $m \approx 2$ obtained in the case of Wollastonite fine powders agrees with the result reported in the literature that its crystals are often in the form of tablets [10].

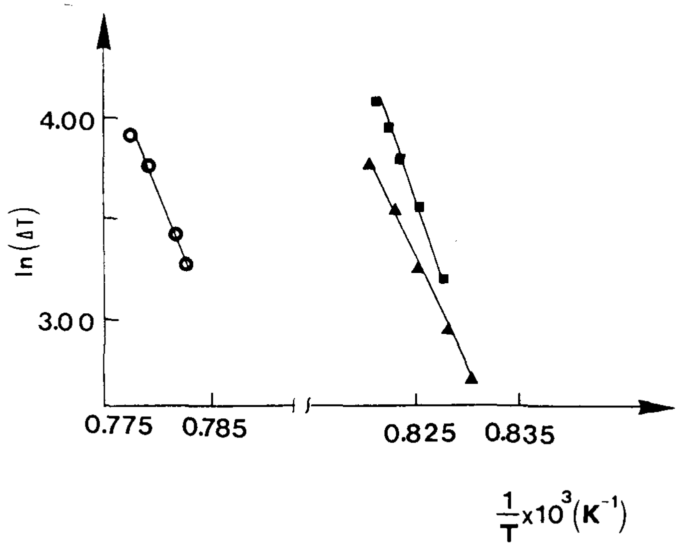

Fig. 5 Plot of $\ln\Delta T$ *vs.* $1/T$ relative to coarse powdered samples (315–500 μm) (symbols as in Fig. 3)

Table 1 E_c and mE_c /kJ·mol^{-1} values of the studied glasses. (c) coarse powders; (f) fine powders

	E_c	mE_c (f)	m_f	mE_c (c)	m_c
$CaO\cdot SiO_2$	653	1548	2.4	1109	1.7
$1.6CaO\cdot 0.4MgO\cdot 2SiO_2$	590	1272	2.2	812	1.4
$1.4CaO\cdot (0.6/3)Y_2O_3\cdot 2SiO_2$	552	1146	2.1	912	1.7

In Fig. 4 the SEM micrographs are reported relative to finely powdered samples sintered and devitrified during a DTA run stopped just after the exo-peak. In Fig. 5 the SEM micrograph are reported relative to small pieces of glasses heated from room temperature till the DTA exo-peak temperature at a heating rate β = 5 deg·min^{-1}. As can be seen, in the case of bulk sample of the MgO substituted glass effectively a columnar crystal growth is observed of nuclei formed on a fracture surface. On the contrary, in the case of the finely powdered samples, a lamellar crystalline structure is observed which well agrees with the value m = 2 found by means of the thermoanalytical techniques. In the

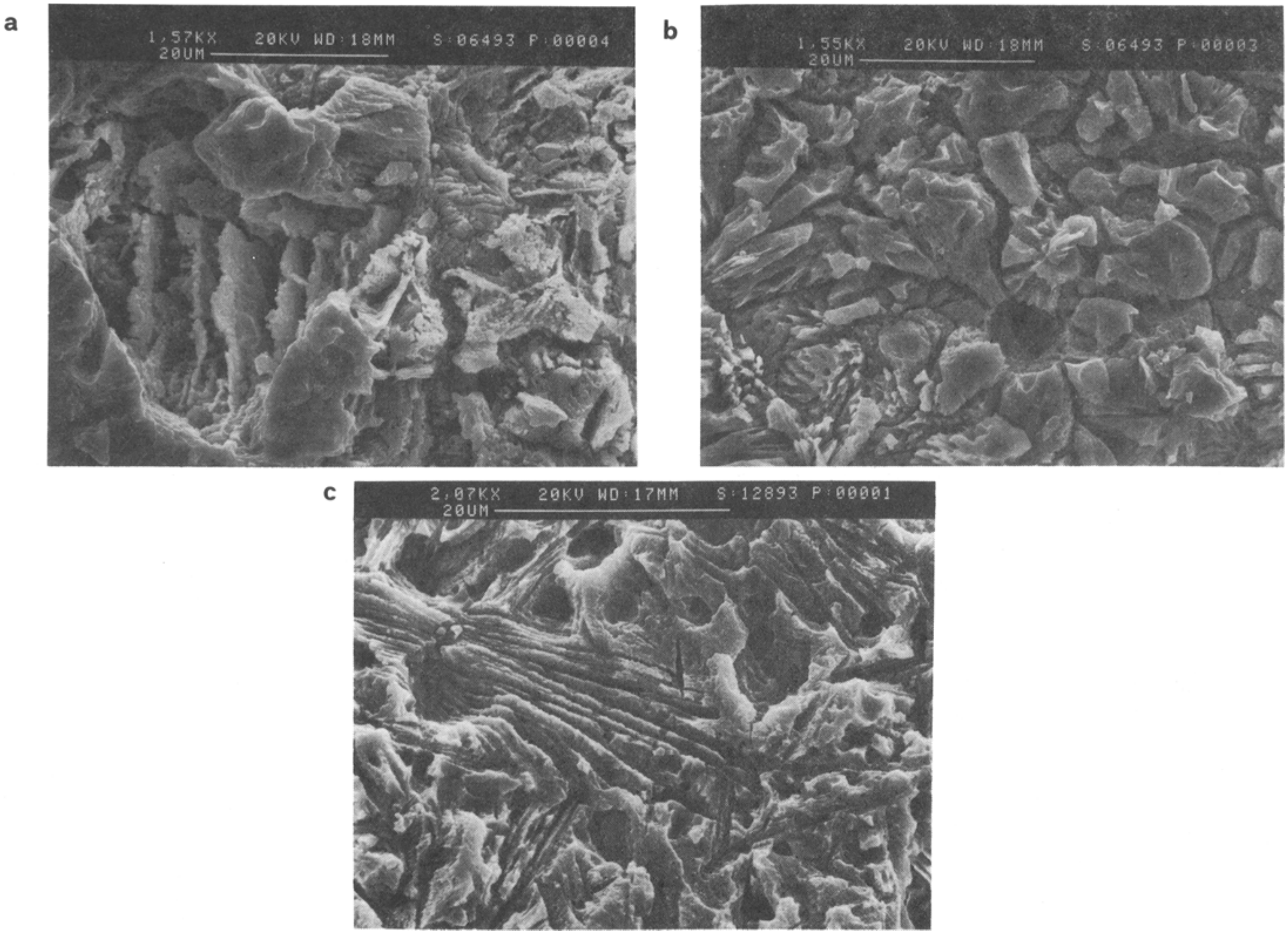

Fig. 6 SEM photographs of finely powdered samples (after a DTA run) relative to CaO.SiO_2 (a), 1.6CaO.0.4MgO.2SiO_2 (b) and 1.4CaO.(0.6/3)Y_2O_3.2SiO_2 (c)

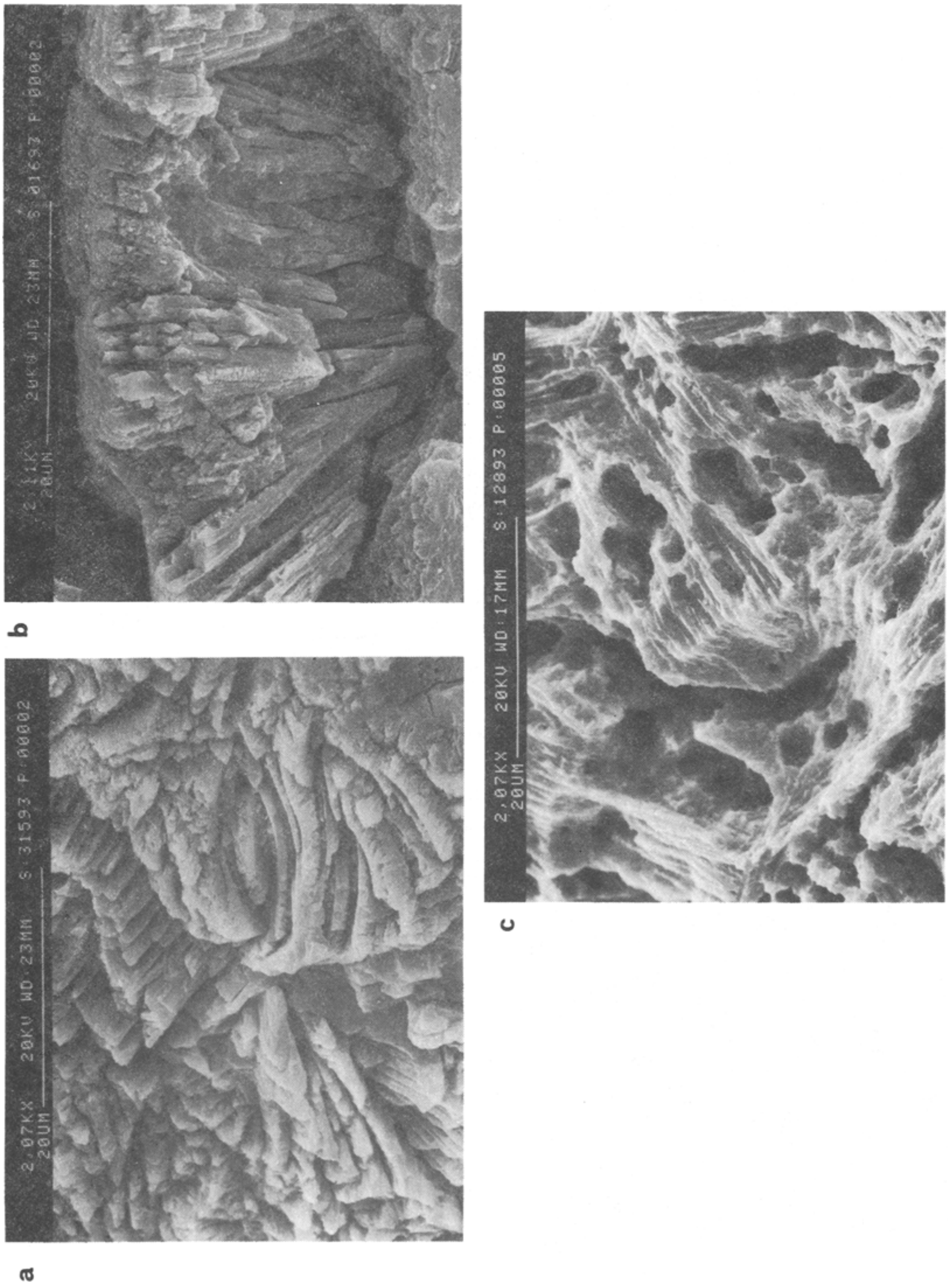

Fig. 7 SEM photographs of bulk samples after a heating cycle at β = 5 deg.min relative to CaO.SiO$_2$ (a), 1.6CaO.0.4MgO.2SiO$_2$ (b) and 1.4CaO.(0.6/3)Y$_2$O$_3$.2SiO$_2$ (c)

other cases a mixed structure is observed consistent with the values $m = 1.6\text{–}1.7$ found in the case of coarse powdered samples.

Conclusions

The studied glasses appear to devitrify by a mechanism involving crystal growth of nuclei preferentially formed on fracture surfaces. Nevertheless surface nuclei can behave as bulk nuclei in powdered samples that sinter before devitrifying; in this case lamellar crystalline structures are obtained.

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Zusammenfassung — Vorliegend wird über eine thermoanalytische Untersuchung der kinetischen Parameter und des Mechanismus des Entglasungsprozesses von $CaOSiO_2$, $1.6CaO\cdot 0.4MgO\cdot 2SiO_2$ und $1.4CaO\cdot(0.6/3)Y_2O_3\cdot 2SiO_2$ berichtet. Die experimentellen Ergebnisse weisen darauf hin, daß in den untersuchten Gläsern ein Oberflächen-Kernbildungsprozeß verläuft; in fein zerpulverten Proben, die vor der Entglasung leicht und wirkungsvoll sintern, verhalten sich die Oberflächenkeime wie Massekeime. In diesem Falle erhält man lamellenartige Kristallstrukturen.