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Thermal behaviour of bioactive alkaline-earth silicophosphate glasses

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The thermal behaviour (sinterability and first crystallization) of a series of alkaline-earth silicophosphate glasses has been studied by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The samples were prepared from a base bioactive glass of the system CaO–P_2O_5–SiO_2–CaF_2, by (a) slightly changing the F/O ratio; (b) replacing part of the CaO by SrO or MgO; and (c) increasing the total alkaline earth concentration by MgO additions. The results show that the addition of MgO is the most effective way of improving sinterability. In these samples, a decrease of the glass transition temperature, together with an increase in the temperature of the first crystallization, is observed. The difference between both temperatures is proposed to be an adequate indicator of the sinterability. The initial stages of the first crystallization (which produces an oxo-fluorapatite), and its composition dependence, are discussed in terms of the results of sinterability, and the classical theory of nucleation.

1. Introduction

Bioactive glass-ceramics are among the most promising materials for clinical use as implants, since they show both remarkable biological and mechanical properties [1–3]. Most of them are calcium silicophosphate based systems, with low concentrations of other components (MgO and CaF_2 in Cerabone™ [2], Na_2O in Ceravital™ [3]). Some of these glass-ceramics are obtained by sintering and crystallization of a powdered glass compact. In these cases sintering takes place by viscous flow at temperatures above the glass transition temperature (T_g).

Viscous sintering can usually proceed up to the crystallization temperature (T_c) [4]. For that reason, Shridaran and Tomozawa have recently proposed that viscosity at T_c might be a good parameter for the estimation of glass-ceramic sinterability [5]. This assumption was supported by viscosity measurements and thermal analysis data obtained from the BaO–SiO_2 system, but, to our knowledge, it has not been tested in other glass systems. The usefulness of this criterion may be limited by the difficulties in obtaining viscosity data at high temperatures (e.g. in the case of small or powdered samples). In these cases, a measure of sinterability in terms of other parameters would be necessary.

In this work, the effect of low concentrations of SrO, MgO and CaF_2 in the sinterability and the first crystallization event (corresponding to the precipitation of an oxo-fluorapatite) of a group of alkaline-earth silicophosphate bioactive glasses is described. These minor components are usually present in these systems, and their effect on the bioactivity and other properties of the materials are still under discussion [6, 7]. One of the aims of this work is to describe the sinterability of these alkaline-earth silicophosphate glasses in terms of easily obtainable thermal parameters.

For this purpose, SEM observations after different thermal treatments, and differential thermal analysis (DTA) of the studied samples were carried. Finally, the dependence of the onset of the apatite crystallization temperature (T_c) with the glass composition is discussed in terms of classical nucleation theory and reported data of related systems.

2. Experimental procedures

Three series of samples were prepared from a base bioactive glass in the system CaO–SiO_2–P_2O_5–CaF_2 [7], by
(a) changing the F/O ratio;
(b) replacing part of the CaO by MgO or SrO; and
(c) increasing the alkaline earth concentration by additions of MgO, without modifying Ca/P, Ca/Si and F/O molar ratios.

The Si/P molar ratio (2.48) was maintained constant in all samples. One of the compositions used in this study corresponds to the apatite–wollastonite glass-ceramic Cerabone™ (sample C3). The compositions of the samples are shown in Table I. The content of CaF_2 in the fluorine-containing samples is between 0.5 and 1 wt %.

The raw materials (MgO, $CaCO_3$, $SrCO_3$, quartz, H_3PO_4 and fluorite) were mixed in the desired stoichiometries, melted at 1400 °C for 240 min, and

TABLE I Batch composition of the glasses used in this study (mol %)

Sample	CaO	MgO	SrO	SiO_2	P_2O_5	RO	F/O
Series A							
A0	54.16	–	–	38.15	7.69	54.16	–
01	54.16	–	–	38.15	7.69	54.16	5×10^{-3}
A2	54.16	–	–	38.15	7.69	54.16	1×10^{-2}
Series B							
B0	47.01	7.15	–	38.15	7.69	54.16	5×10^{-3}
01	54.16	–	–	38.15	7.69	54.16	5×10^{-3}
B2	47.01	–	7.15	38.15	7.69	54.16	5×10^{-3}
Series C							
01	54.16	–	–	38.15	7.69	54.16	5×10^{-3}
C3	50.29	7.15	–	35.42	7.15	57.44	5×10^{-3}
C4	46.79	13.61	–	32.96	6.64	60.40	5×10^{-3}
Sample Q2	52.15	3.70	–	36.74	7.41	55.85	5×10^{-3}

poured on to a steel plate. A sample which was quenched in water (sample Q2) was also included, although its thermal behaviour cannot be compared to that of the others due to its different thermal history. The reasons for its inclusion will be discussed later. After each different thermal treatment, the crystalline phases were identified by XRD analysis. Characterization of some multiphased samples was completed by ^{29}Si and ^{31}P NMR (nuclear magnetic resonance) analysis [8].

DTA of glass bulk samples were carried out at a heating rate of 10 °C/min with a Mettler H51 station. No previous nucleating treatments were carried out before the runs. The results of these analyses are shown in Table II.

For the analysis of sinterability, samples were sieved through a 325-mesh screen, put on a flat disc without previous compaction, and subjected to different thermal treatments at temperatures between 800 and 1130 °C. Electron microscopy photographs were taken of the samples subjected to an isothermal treatment at 900 °C for 1 h.

3. Results

3.1. Differential thermal analysis

The DTA curves (Fig. 1a, 1b and 1c) show that all the glasses used in this study present at least two exothermic events on heating the samples to temperatures higher than T_g. The first one, at temperatures near 900 °C, is attributed to the crystallization of oxofluoroapatite ($Ca_{10}P_6O_{24}$ $[O, F_2]$), as was also reported by Kokubo *et al.* [2] and Shyu *et al.* [9] for related compositions.

At higher temperatures, crystallization of β-wollastonite ($CaSiO_3$) occurred, except in the case of sample C4, where diopside ($CaMgSi_2O_6$) crystallized [8, 10].

In the magnesium-containing samples a third exothermic event was observed at about 1160 °C. This event was reported to be related, in the case of sample C3, to the transformation of apatite into β-tertiary calcium phosphate, also called β-TCP ($Ca_3[PO_4]_2$) [2].

Two characteristic temperatures can be obtained from the DTA curves, and both are included in Table II: the glass transition temperature (T_g) and the temperature of the onset of the first exothermic event (apatite crystallization), which will be called T_c. The temperatures of the maxima of the peaks (T_p) show a similar trend with composition (Fig. 1) and are not included in the table.

TABLE II Glass transition (T_g), apatite crystallization (T_c), and apatite–β-TCP transformation (T_w) temperatures obtained from DTA runs (all values correspond to the beginning of each event) (°C)

Samples	T_g	T_c	T_w	$\Delta T (T_c - T_g)$
Series A				
A0	773	908	–	135
01	768	877	–	109
A2	753	870	–	116
Series B				
B0	735	848	1136	113
01	768	877	–	109
B2	734	869	–	135
Series C				
01	768	877	–	109
C3	731	882	1136	151
C4	725	889	1135	164
Sample Q2	751	904	1156	153

In series A, a decrease of T_g in the F-containing samples can be observed, a phenomenon which has been widely reported in silicate glasses. The effect arises from the partial substitution of oxygen by fluorine (both having similar ionic radii), which results in a decrease in viscosity due to the rupture of Si–O–Si bonds [11], and may be the reason for the observed results. The fluorine effect is more remarkable in the first crystallization step: substitution of only 1.6% of the CaO present in sample A0 by CaF_2 (sample A2) lowered the value of T_c by more than 30 °C.

In the case of series B, the replacement of 13 mol % of CaO in sample 01 by SrO and MgO (samples B2 and B0, respectively) decreased the value of T_g. With respect to T_c, the value for sample B0 is lower than that for samples 01 and B2.

Finally, in series C, additions of MgO resulted in a decrease in T_g from sample 01 to C4. Table II also shows that T_c increases slightly from sample 01 to sample C4.

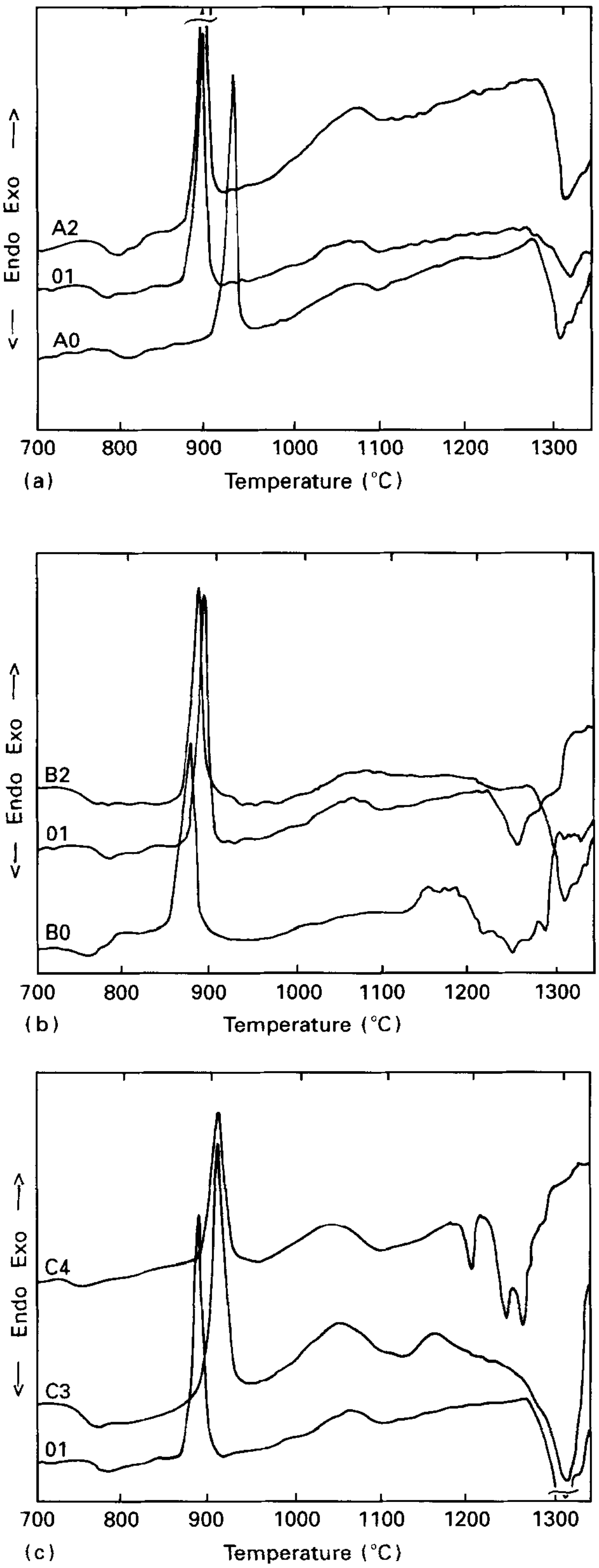

Figure 1 DTA curves at 10 °C/min of the glass samples of (a) series A; (b) series B; (c) series C.

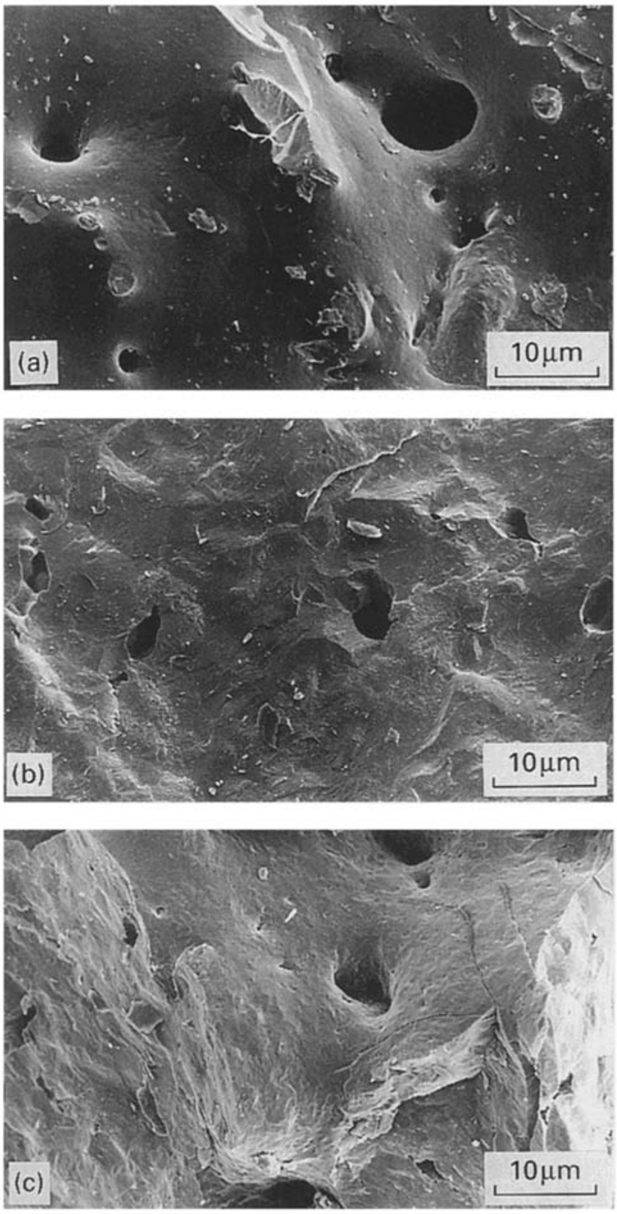

Figure 2 SEM micrographs of the glass samples: (a) Q2; (B) C3; and (c) C4, sintered at 900 °C for 1 h (Group I).

3.2. Scanning electron microscopy

Figs 2, 3 and 4 show the morphology of all the samples of this study after being subjected to an isothermal treatment at 900 °C for 1 h. The samples were previously sieved through a 325-mesh screen in order to avoid any particle size effect, put on a flat Pt disc without previous compaction, and sintered. From the analysis of the photographs we can distinguish three groups of samples (I, II and III) with different morphologies.

Samples belonging to group I (Q2, C3 and C4) are clearly sintered by viscous flow. In every case a strong monolithic piece was formed, which had to be broken for observation. A smooth microstructure can be observed in Fig. 2. In these samples it is impossible to distinguish the initial particles.

The particles of samples B2 and A0 (group II) showed agglomeration and sticking between them after the thermal treatment, but the shape of the particles did not change so much. Although again in this case a single piece resulted from the heat treatments, the viscous flow phenomena was less pronounced than that observed in group I: the samples were easily broken, and the size of the particles was almost equal to that of the initial compact (Fig. 3); however, the rounding of their edges is noteworthy. Fig. 3 also shows the existence of necks between the particles.

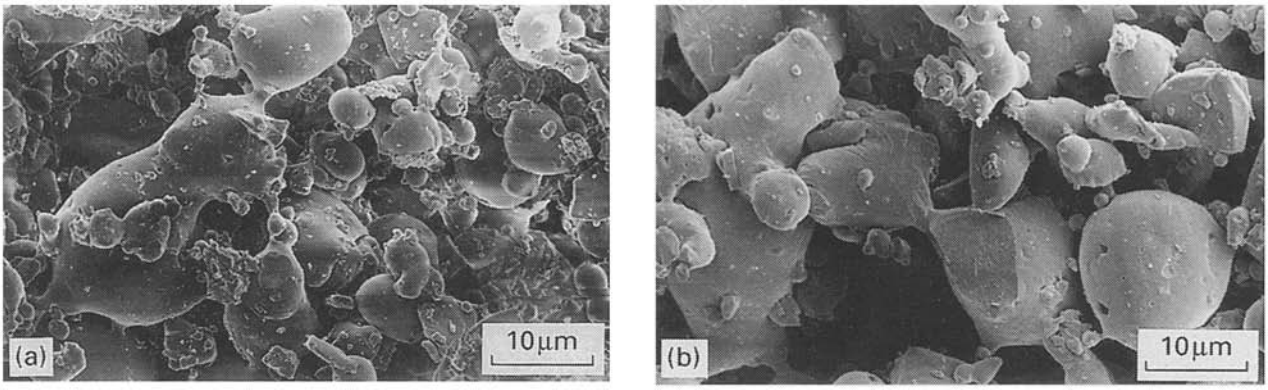

Figure 3 SEM micrographs of the glass samples: (a) A0; and (b) B2, sintered at 900 °C for 1 h (Group II).

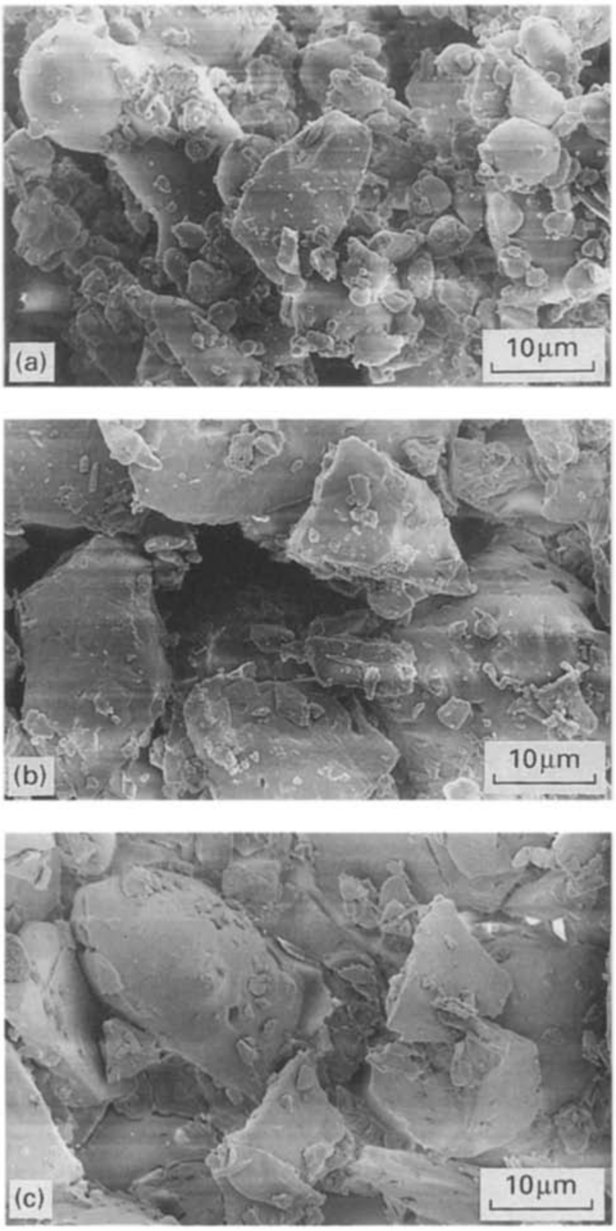

Figure 4 SEM micrographs of the glass samples: (a) 01; (b) B0; and (c) A2, sintered at 900 °C for 1 h (Group III).

Samples A2, 01 and B0 (group III) remained as loose powders (Fig. 4). Thermal treatments did not result in monolithic pieces, and the size and shape of each particle is similar to that of the initial powder.

It is important to remark that these three groups of samples were also observed after subjecting the glass powders to many different isothermal and non-isothermal treatments, between T_g and 1130 °C. In all the cases, each group included the same samples.

4. Discussion

4.1. Sinterability

According to the observed behaviour and the results shown in Table II, it can be noted that the sinterability of the samples is enhanced when the values of T_g are reduced and the values of T_c are increased, i.e. when the values of ΔT ($T_c - T_g$) are higher. Samples Q2, C3 and C4 (group I) present values of ΔT higher than 150 °C. In the case of group II, ΔT of the samples is about 135 °C. Finally, in group III, the values of ΔT of each sample are lower than 110 °C.

At this point, the convenience of using the temperature of the onset of crystallization (T_c, Table II) instead of the temperature of the peak maximum (T_p) is demonstrated, since, as was mentioned above, the inhibition of sintering begins at T_c [4, 5].

These results show that the partial replacement of CaO by MgO does not promote viscous flow phenomena. On the other hand, the addition of MgO, which led to an increase in the total alkaline earth content of the system, results in the most effective method of improving sinterability.

The results also show that the difference between T_c and T_g (ΔT) can be taken as an indicator of the sinterability of these samples. The relation between sinterability and ΔT is still valid even in the case of sample Q2, although its thermal history (and, as a consequence, many of its properties) is different to that of the rest of the samples.

Among all the parameters which must be considered in sintering or densification kinetics of glasses [11–13], only surface free energy and viscosity (η), depend on the composition of the system. These parameters are of interest in this study, since the particle sizes of the glasses were similar in all samples (all were sieved through a 325-mesh screen before the thermal treatments). Surface energy variations with temperature and composition are small compared with those of viscosity [5, 14]. Thus, the observed variation in sinterability among the studied samples is probably due to variations on the viscosity of the system at the studied temperatures.

If we assume that the value of viscosity at T_g is constant, the observed results can be interpreted in terms of the effect of compositional changes on:

(i) the temperature dependence of viscosity between T_g and T_c; and
(ii) the value of viscosity at T_c.

According to this, only four possible situations are likely to occur, and will be considered as follows:

(a) *The value of viscosity at* T_c *and the temperature dependence of viscosity between* T_g *and* T_c *are similar in all the samples.* If this were the case, T_g and T_c would change with composition in the same way. Table II shows that this is clearly not the case in groups II and III: in both cases, T_g decreases while T_c increases.

(b) *There is a different temperature dependence of viscosity in each sample, but the values of viscosity at* T_c *are similar.* In this case, the only possible justification for the observed results would be related to differences in the time during which the sintering takes place. For example, samples with similar T_g and different T_c (e.g. samples B0 and B2) would sinter in the same range of viscosity values, but the sample with higher T_c would have more time for this process to occur. This argument could explain the different sinterability of these samples after being subjected to non-isothermal treatments. But isothermal treatments would show no differences in the sintering behaviour of both samples. Fig. 2 shows the behaviour of the samples after an isothermal treatment at 900 °C, and clearly demonstrates that this assumption is incorrect.

Then, the two remaining possibilities to be considered are:

(c) *Both the temperature dependence of viscosity, and its value at* T_c*, are dissimilar in the different samples,* and

(d) *The temperature dependence of viscosity is similar in all the samples and the values of viscosity at* T_c *are not the same.*

Both hypotheses imply that the value of viscosity at T_c is different in each sample. Although the results do not allow us to determine the correct one, the strong correlation observed between ΔT and sinterability suggests that the samples with higher ΔT are the ones which present the lowest values of viscosity at T_c. This means that either (c) is true, or the temperature dependence is more pronounced in the samples with higher ΔT. Anyway, any of these conclusions show that:

(a) the proposed criteria of sinterability (i.e. the value of ΔT) does not disagree with Sridharan and Tomozawa's criterion [5], proposed for a series of SiO_2–BaO based glasses; and
(b) viscosity is not the controlling factor in the first stages of apatite crystallization.

The last topic will be discussed in more detail in the next section.

4.2. Apatite crystallization

In a previous work [16] the authors found that the crystallization mechanism of apatite is clearly homogeneous (the sharp DTA exothermic peak in Fig. 1 is also a characteristic associated with this phenomenon), in agreement with previously reported data in related systems [2, 9]. In this work, the effect of composition on the crystallization behaviour of apatite will be analysed. No non-isothermal kinetic equations [17–19] are used to discuss the thermal analysis data, since:

(a) the composition of the glassy phase is not constant during the crystallization of apatite; and
(b) no previous nucleating treatments were made, so the number of nuclei is not constant during crystallization.

For this reason, the kinetic parameters E_a and N, which could be obtained from these equations, probably do not have a defined physical meaning.

However, inasmuch as the initial number of nuclei should be close to zero (no pre-nucleating treatments were carried out before the runs), we assume that an increment in the initial nucleation rate at a fixed temperature between T_g and T_c would imply a reduction in the value of T_c.

A qualitative analysis of the composition dependence of the nucleation rate in glasses (v_n) can be done [20], in terms of the classical theory of nucleation. A similar composition dependence is expected for the value of T_c. Isothermal homogeneous nucleation kinetics can be described by

$$v_n = A\exp[-(\Delta G_{\max} + E_D)/RT] \qquad (1)$$

where

A = frequency factor = $n_v(RT/h)$
$\Delta G_{\max}$ = $16\pi\sigma^3/3(\Delta G)^2$
ΔG = molar bulk free energy change in crystallization per unit volume
E_D = activation energy of diffusion
σ = crystal–liquid interfacial free energy per unit area
n_v = number of formula units of the crystallizing component phase per unit volume

E_D strongly depends on viscosity (η) [5, 20], according to

$$D = (RT\lambda^2/h)\exp(-E_D/RT) = RT/3\pi\lambda\eta \qquad (2)$$

where λ is the "jump distance" and η depends on temperature according to [15]

$$\log\eta = A + B/(T - T_0) \qquad (3)$$

(A, B and T_0 are material constants).

From these equations, we can observe that the parameters which can greatly decrease the rate of nucleation and, as a consequence, increase the value of T_c, are: viscosity, σ, $\Delta G_{\max}$ ($\propto 1/\Delta G$), and, perhaps to a minor extent, the number of components of the glass (included in A). Except for σ, all of these are highly compositional dependent. But one point which was concluded from Section 4.1 must be remembered: in the first stages of apatite crystallization, viscosity is not the controlling factor, of this phenomenon. Thus, variations in ΔG with composition must be taken into account in this system, in order to discuss the values of T_c. Recently, it was reported, for a related glass system

[9], that ΔG is the controlling factor of the nucleation rate of apatite.

An estimation of ΔG in complex glasses, as suggested by James [20], can be done in a similar way to that in the case of a binary system. In this way, ΔG is proposed to have a maximum for a glass composition at or near the corresponding crystalline phase. According to this approach, Shyu *et al.* [9] proposed, for a magnesium calcium silicophosphate glass system which crystallizes into apatite, that ΔG is proportional to:

(a) the Ca and P content of the glass; and
(b) the similarity between the Ca/P molar ratio of the glass and that of the crystalline phase (1.67 for apatite).

In the case of series B, a higher value of ΔG in sample B0 with respect to sample 01 is expected if the latter criterion is adopted. This is in agreement with the observed decrease in T_c from sample 01 to sample B0. With respect to sample B2, although the Ca/P ratio is equal to that of sample B0, it presents a higher T_c. However, the criterion of the molar ratios can also be applied if we take into account the following considerations. According to a previous work [10], solubility of Mg in this type of apatite is rather low (about 1 wt %). In contrast, it was found that all the Sr contained in sample B2 is present in the apatite structure after the first crystallization step. On account of the complete solubility of Sr in apatite, in this case, the molar ratio to be considered is M/P ($M = \mathrm{Ca} + \mathrm{Sr}$). This ratio is the same for samples 01 and B2, and is lower in the case of sample B0. This may be the reason why samples 01 and B2 show a similar value of T_c, which is higher than that of sample B0.

However, Shyu *et al.* [9] observed that substitution of Ca by Mg increased T_c, and explained this result by means of the decrease in the content of Ca. By considering this data together with our results, it seems that the proposed criteria to estimate the relative values of ΔG present limitations when both the Ca and P contents and the Ca/P molar ratio are modified.

In the case of series C, Table II shows that T_c increases slightly from sample 01 to sample C4, in spite of the fact that T_g decreases in the same direction. Again in this case, the ΔG approach could be used, according to the previous discussions. In this series, Ca/P ratio is constant. Then, it could be possible to relate the variations in ΔG to the Ca and P content. As a result of the MgO additions, the total amounts of Ca and P decrease from sample 01 to C4. An increase in the value of ΔG can then be expected, leading to the observed shift of T_c to higher temperatures. But care must be taken when using this approach, since in this case, the content of each of the glass components is changing along the series.

In the case of series A, Fig. 1 and Table II show a reduction of 30 °C in the value of T_c due to the substitution of only 1.6% of the CaO present in sample A0 by CaF_2 (sample A2). In agreement with this data, Kokubo *et al.* reported a decrease in T_c [21] when increasing both Ca and F content by the addition of 0.5 wt % of CaF_2 to similar glass.

Although the lowering of the value of T_g by the addition of F could justify the observed decrease in T_c, through a reduction of the glass viscosity near T_c, again in this case the effect of the free energy change (ΔG) on T_c must also be taken into account.

It was observed that although the content of F is quite low (see Table I), all the added F is present in the apatite phase after crystallization [2, 10]. This means that the effect of the fluorine content on the free energy of apatite is probably more relevant than its effect on the free energy of the parent glass. Then, a different approach to estimate variations in ΔG is needed, in which ΔG is more likely to be related to changes in the free energy of crystalline apatite, rather than the free energy of the glass. In this respect, stabilization of hydroxyapatite was reported to occur by the substitutions of OH by F [22]. Then, the reduction in T_c could be explained not only by a decrease in viscosity of the glass, but also by an increase in ΔG which is related to the stabilization of apatite.

5. Conclusions

The values of T_g in the studied glasses decreased with (a) the molar ratio F/O; (b) the partial substitution of Ca by Mg or Sr; and (c) the addition of MgO. With respect to T_c, its value increased with the addition of MgO, and decreased with (a) the molar ratio F/O and (b) the partial substitution of Ca by Mg.

Viscous sinterability of the samples is enhanced when the values of T_g are reduced and the values of T_c are increased, i.e. when the values of ΔT ($T_c - T_g$) are higher. The value of ΔT is proposed to be a good indicator of the sinterability of the system.

The addition of MgO, which led to an increase in the total alkaline earth content of the system, resulted in the most effective method of improving sinterability by viscous flow. For this reason, dense glass-ceramics can be only obtained from glass powder compacts of samples Q2, C3 and C4.

The proposed criteria of sinterability (the value of ΔT) does not disagree with Sridharan and Tomozawa's criterion, proposed for a series of SiO_2–BaO based glasses, since it was deduced that the value of viscosity at T_c must be different in each sample.

Viscosity is not the controlling factor in the first stages of apatite crystallization. The analysis of the crystallization behaviour at this stage in terms of classical nucleation theory suggests that ΔG is the controlling factor of the initial crystallization rate of apatite.

An estimation of the relative variation in ΔG with composition from the Ca/P molar ratio, and the amount of Ca and P, as was recently proposed for a related system, presents limitations when:

(a) both parameters are changing together;
(b) the content of the other components are changing as well;
(c) ΔG variations are related to modifications on the free energy of the crystal rather than the corresponding value of the glass.

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