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Effects of composition on crystallization behaviour and mechanical properties of bioactive glass-ceramics in the MgO–CaO–SiO_2–P_2O_5 system

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Abstract

The effects of replacement of P_2O_5 by SiO_2, on the crystallization behaviour, mechanical properties and bioactivity of glass-ceramics in the MgO–CaO–SiO_2–P_2O_5 system were investigated. By decreasing P_2O_5 and increasing SiO_2, the apatite crystallization peaks disappeared from DTA traces, whereas the wollastonite peaks remained unchanged. XRD results showed that by decreasing P_2O_5 and increasing SiO_2 contents, the amount of apatite and wollastonite phases were decreased and increased, respectively. The diametral compression strength (DSC) and indentation fracture toughness (IFT) values gradually raised with increasing wollastonite content. The best results obtained for the specimens with the maximum amount of wollastonite were 36.6 and 2.74 MPa $m^{1/2}$ for DCS and IFT, respectively. The bioactivity of specimens after being soaked in a simulated body fluid for one month were examined by SEM/EDX and FT–IR. A thin apatite layer was formed even on the surface of specimens containing the minimum amount of apatite phase. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Mechanical properties; D. Glass ceramics; Composition; Crystallization; MgO–CaO–SiO_2–P_2O_5

1. Introduction

It has been reported [1–4] that some glass-ceramics in the MgO–CaO–SiO_2–P_2O_5 system, containing apatite and β-wollastonite phases, with good mechanical properties and the ability of forming tight chemical bonds with living bone [1,4,5] can be produced through sintering and subsequent crystallization of glass powders. The effect of compositional changes on the bioactivity [6] and the crystallization behaviour of some glass-ceramics located in certain compositional regions of the system has also been investigated [7].

The main objective of the present investigation is to study the effect of P_2O_5 replacement by SiO_2 on the mechanical properties of the above mentioned glass-ceramics.

The effect of these composition changes on the crystallization behaviour of these materials, in relation to their mechanical properties was also investigated.

2. Experimental procedure

2.1. Sample preparation

The glass composition reported by Kokubo et al. [2]. was chosen as the basic composition in this investigation and changes were made in it by replacing P_2O_5 by SiO_2 in 3 wt% steps. The glass compositions are shown in Table 1. The batch mixtures were prepared from reagent grade MgO, $CaCO_3$, H_3PO_4 and pure quartz sand. The batches were melted in platinum crucibles in the 1450–1490°C range, according to their composition. Table 2 shows the suitable melting conditions to obtain clean, bubble free and quite fluid melts. Glass powders were obtained by pouring the melts onto a stainless plate and subsequent pulverizing them in a planetary mill for 5 h, using a zirconia lined jar and zirconia balls. Fig. 1. shows the particle size distribution of glass powders after milling. The powders after thorough mixing with a binder and granulation, were pressed into discs 22.8 mm in diameter and 5 mm thick.

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Table 1
Chemical composition of prepared glass, wt-%

Oxide	Glass G_1	Glass G_2	Glass G_3	Glass G_4
SiO_2	34.2	37.2	40.2	43.2
CaO	44.9	44.9	44.9	44.9
MgO	4.6	4.6	4.6	4.6
P_2O_5	16.3	13.3	10.3	7.3

Table 2
Melting conditions

Glass composition	Melting temperature (°C)	Melting time (h)
G_1	1450	2
G_2	1460	2
G_3	1470	2
G_4	1490	2

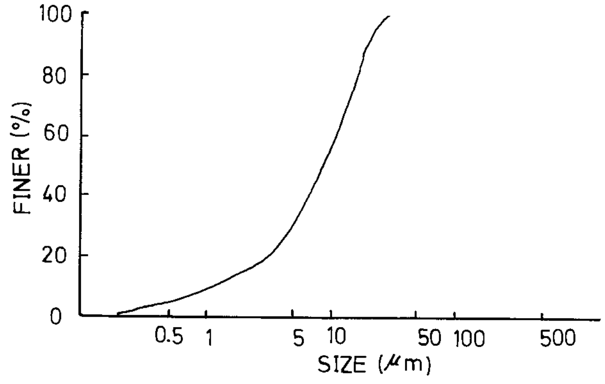

Fig. 1. Typical particle size distribution of powders after 5 h of milling.

2.2. Thermal measurements

To determine the suitable heat treatment conditions, differential thermal analysis (DTA) was performed on glass powders at a rate of 10 K/min using alumina powder as an inert reference material.

2.3. Phase identification and microstructural analyses

Crystalline phases formed in the heat treated specimens were identified by powder X-ray diffractometry (XRD) and their microstructures were observed under a scanning electron microscope (SEM). For SEM observations the fractured surfaces of samples, after etching in 0.5 M HCI solution for 10–30 s, were coated with a thin layer of gold.

2.4. Measurement of mechanical properties and bioactivity

The strength and fracture toughness of specimens were determined by diametral compression [8,9] and indentation fracture [10–15] methods, respectively. For diametral compression, the glass and glass-ceramic specimens in the form of disks, after grinding and polishing were subjected to a compressive stress along their diameter. The cross-head speed was 2.5 mm/min. At least 5 measurements were made to obtain one data point. In the case of indentation fracture test, again well polished specimens were subjected to a Vickers indenter under an optimum load of 10–20 N and 20–30 N for glass and glass-ceramics, respectively.The holding time after an indent was 3 min. Data were obtained using at least 5 indentations on each specimen.

In order to evaluate the bioactivity of specimens, they were immersed in a simulated body fluid (SBF). The SBF was prepared and used according to the procedure described by Kokubo et al. [16,17]. Some specimens after soaking in the SBF for one month were examined by SEM/EDX (energy dispersive X-ray analysis) in order to determine the thickness and composition of the layer formed on their surfaces.

3. Results and Discussion

3.1. The crystallization behaviour of glasses

Fig. 2. shows the DTA traces for specimens G_1–G_4. It can be seen that while specimens G_1 and G_2 show double exothermic peaks, specimens G_3 and G_4 exhibit only a single peak. These peaks are usually attributed to the crystallization of glassy specimens. In order to identify the products of the crystallization processes, each specimen was heated up and kept at its respective crystallization temperature in an electric furnace, for 4 h. Fig. 3(a,b). represents typical XRD results for specimens G_1 and G_4. It was revealed that the first exothermic peaks for specimens G_1 and G_2 can be attributed to the crystallization of apatite (oxyapatite), whereas the second peaks represent the crystallization of wollastonite. The single exothermic peaks in the case of specimens G_3 and G_4 are also due to the crystallization of wollastonite. The exothermal effect of crystallization of apatite in the case of the latter specimens has been masked over by the wollastonite peaks and are not detectable. In order to examine the relatively weak exothermal effects detectable in some specimens in the 1150–1200°C range, (Fig. 2) it was decided to keep all specimens at 1200°C for 4 h.

Fig. 3c shows the result for specimen G_4. It can be seen that heating the specimens at 1200°C resulted in a new crystalline phase, whitlockite (β-$3CaO{\cdot}P_2O_5$). These results are consistent with results of other investigators [4,5].

Table 3 summarizes the DTA and XRD results. It can be concluded that the replacement of P_2O_5 by SiO_2 increases the crystallization temperature of apatite (first DTA peaks for specimens G_1 and G_2) whereas the

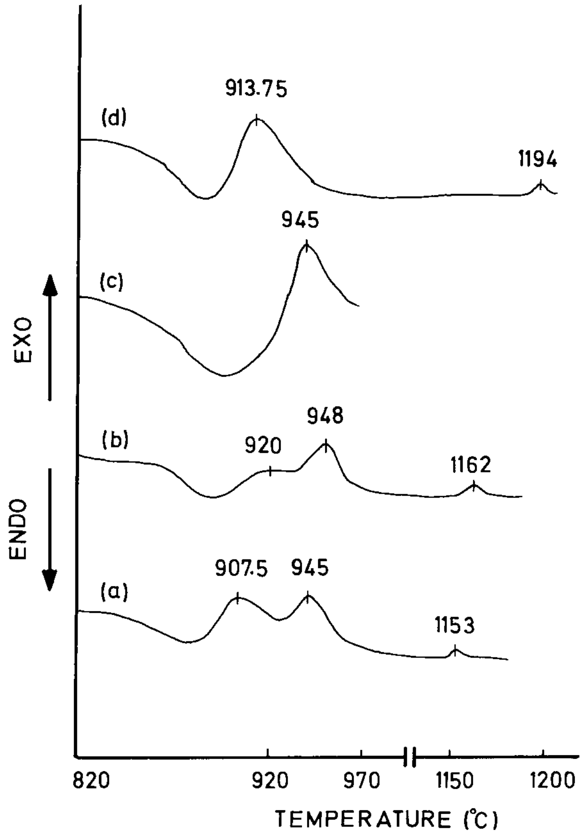

Fig. 2. DTA traces for specimens (a)G_1, (b)G_2, (c) G_3 and (d)G_4.

crystallization temperature of wollastonite in the case of specimens G_1–G_3 remained almost unaffected. A further increase in the content of SiO_2 from specimen G_3 to G_4 caused a marked decrease of this temperature. From Fig. 4 it can be seen that in the case of specimens heat treated at their respective second exothermic peaks, increasing the content of SiO_2 at the expense of P_2O_5 caused a gradual decrease in the amount of apatite whereas the amount of wollastonite steadily increased.

Fig. 5 shows that in the case of specimens heat treated at 1200°C a gradual increase in wollastonite and decrease in whitlockite occurred with increase of SiO_2 content.

3.2. Mechanical peroperties

Fig. 6 represents the results of a diametral compression strength (dsc) test. It can he concluded that the decrease of P_2O_5 (which led to the increase of wollastonite content) increased the dsc values. It is believed that by the dsc method more representative and reliable results can be obtained concerning the tensile strength of brittle materials compared to the more widely used methods such as three point bending tests [8,9]. As in the case of the latter test, only the surface of specimens is subjected to the maximum tensile stress, so the surface defects make a great contribution to the strength values, whereas in the dcs method, the bulk of material is subjected to tensile stresses. Therefore in the case of the dsc test, considerably lower strength values can be expected.

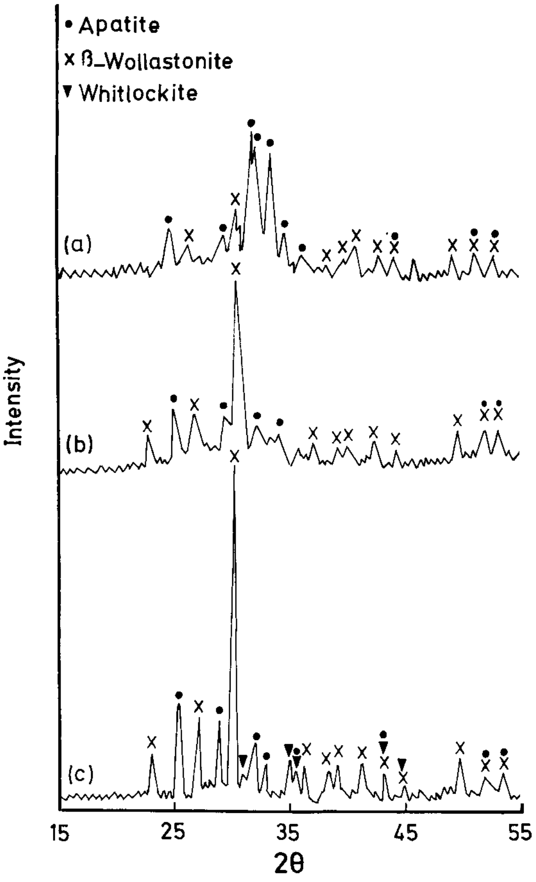

Fig. 3. XRD patterns for specimens (a) G_1 crystallized at 945°C, (b) G_4 crystallized at 914°C and (c) G_4 crystallized at 1200°C.

Table 3
DTA and XRD results

Sample No	First exo. peak/cryst. products	Second exo. peak/cryst. products	Cryst. products at 1200°C
G_1	907°C/A[a]	945°C/A + W	A + W + C_p[c]
G_2	920°C/A	948°C/A + W	A + W + C_p
G_3	945°C/A + W[b]	—	A + W + C_p
G_4	914°C/A + W	—	A + W + C_p

[a] A = apatite.
[b] W = wollastonite.
[c] C_p = whitlockite.

From Fig. 7 it can be deduced that the replacement of P_2O_5 by SiO_2 increased the indentation fracture toughness values of glass-ceramics, whereas in the case of glassy specimens it was almost ineffective. This can be related to the gradual increase of the wollastonite phase caused by the compositional changes.The wollastonite phase, which has a fibrous morphology may enhance the fracture toughness by several mechanisms such as crack deflection and crack bridging. Fig. 8, which has been taken from the fractured surface of specimen G_1 after heat treatment at 1200°C, clearly shows the fibrous morpholgy of the wollastonite crystals.

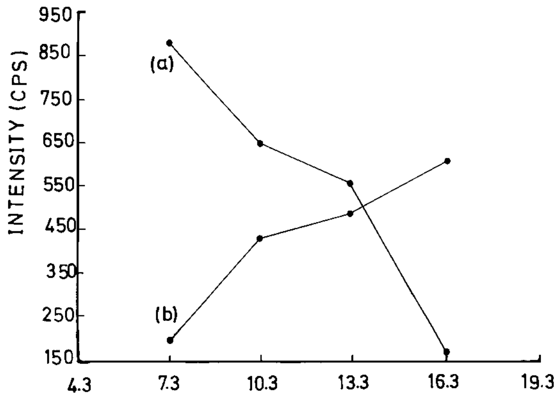

Fig. 4. The main XRD peak heights of (a) wollastonite (320) and (b) apatite (211) vs wt% P_2O_5 after heat treatment at the second exothermic peaks for 4 h.

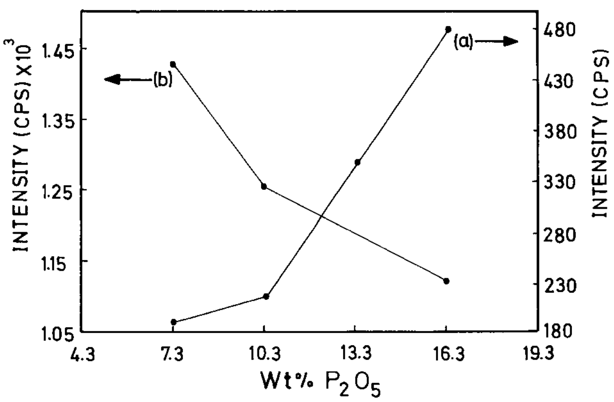

Fig. 5. The main XRD peak heights of (a) whitlockite and (b) wollastonite (320) vs wt% P_2O_5 after heat treatment at 1200°C for 4 h.

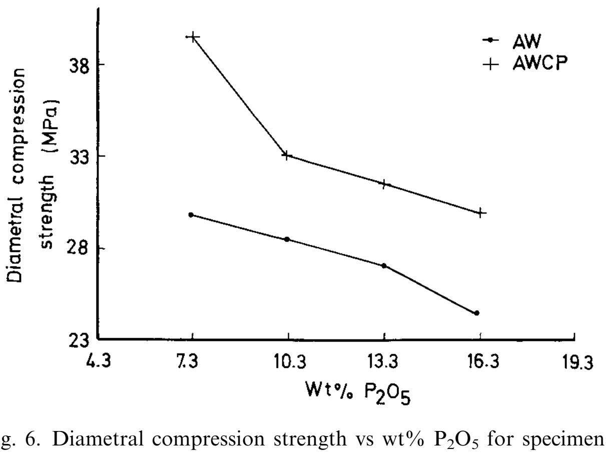

Fig. 6. Diametral compression strength vs wt% P_2O_5 for specimens, (AW) heat treated at the second exothermic peaks and (AWCP) heat treated at 1200°C.

3.3. Effect of soaking in the simulated body fluid (SBF)

According to Kokubo et al. [16] the formation of an apatite layer on the surface of a specimen after immersion in a SBF is an indication of its ability to form tight chemical bonds with natural bone (bioactivity).

The immersion result of specimen G_4 (crystallized at 1200°C for 4 h) in SBF for one month showed that a layer, approximately 15 µm thick, has been formed at the surface of this specimen, which was almost twice that, as compared to the specimen examined by Kokubo et al. [17]. Therefore, it can be concluded that contrary to earlier assumptions, the decrease of P_2O_5 content in the glass specimens and the subsequent decrease in apatite phase in glass-ceramics, has not impaired the bioactive characteristic of these materials, but probably has even enhanced their bioactivity. This is

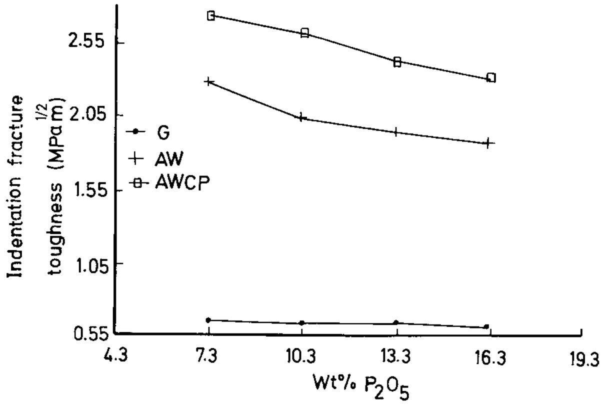

Fig. 7. Indentation fracture toughness vs wt% P_2O_5 for specimens, (g) glass, (AW) heat treated at the second exothermic peak and (AWCP) heat treated at 1200°C.

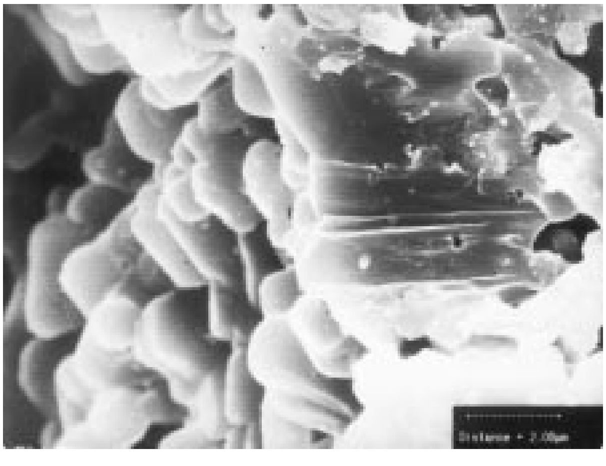

Fig. 8. SEM micrograph for specimen G_1 after heat treatment at 1200°C for 4 h (fractured surface).

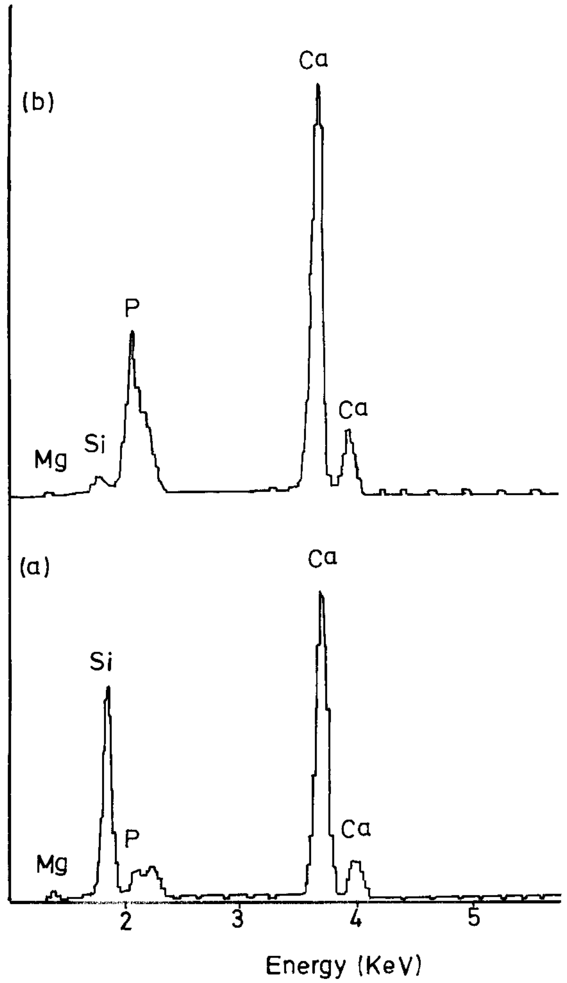

Fig. 9. EDX spectra for (a) glass-ceramic matrix and (b) the layer formed on the specimen surface after one month of immersion in SBF.

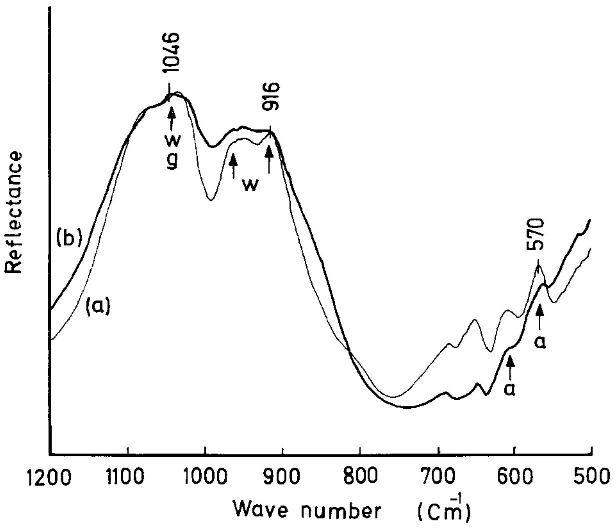

Fig. 10. FT-IR traces for (a) after immersion and (b) before immersion of specimens in SBF.

consistent with results of Kokobu et al. [17,18] which indicated that the essential condition for a glass-ceramic to form a tight chemical bond with living bone is not the existence of an apatite phase within it, but the ability of it to develop a thin apatite surface layer in a body environment. It is also consistent with findings of Kasuga et al. [6]. indicating that the replacement of P_2O_5 by SiO_2 increases the amount of apatite phase in the surface layer of these glass-ceramics after immersion in SBF.

In order to determine the chemical composition of the layer, the glass-ceramic matrix and the layer were analyzed by EDX. The result shown in Fig. 9 indicates relatively higher content of P and Ca elements in the layer compared to the matrix, which can be taken as evidence for the presence of a higher concentration of apatite crystals in the layer. Fig. 10 shows the Fourier transform infrared reflection spectra (FT-IR), taken from the crystallized G_4 specimen, before and after one month of immersion in SBF. It can be seen that the reflectances at wavenumbers 570 and 605 cm^{-1} which correspond to the P-O [19] has been raised after immersion in SBF, which may be an indication of an increase in apatite phase.

4. Conclusions and suggestions for further work

1. By increasing the amount of SiO_2 at the expense of P_2O_5, the amount of apatite precipitated in glasses was decreased and its formation temperature was raised, whereas the content of wollastonite was increased and its formation temperature first remained almost constant and then was decreased.
2. The content of whitlockite (β -3CaO·P_2O_5) which was formed in all specimens at 1200°C, was decreased by decreasing content of P_2O_5.
3. The diametral compression strength and indentation fracture toughness values were raised by increasing content of SiO_2 at the expense of P_2O_5, which can be attributed to the increase of wollastonite.
4. The fibrous morpholgy of the wollastonite crystals, observed by SEM, is responsible for its positive effect on mechanical properties of these glass-ceramics.
5. The specimens containing the minimum amount of P_2O_5 (which were the strongest and toughest ones) form an apatite layer on their surface, after immersion in SBF, which is an evidence of their bioactivity.
6. Since it was proved that the presence of apatite has a detrimental effect on the mechanical properties of these glass-ceramics and on the other hand it was confirmed that the presence of this phase is not essential for the bioactive characteristic, so we suggest that further reduction (or probably complete exclusion) of P_2O_5 from the composition of these glass-ceramics could increase the strength and toughness.

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