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HA forming ability of some glass-ceramics of the $CaMgSi_2O_6$–$Ca_5(PO_4)_3F$–$CaAl_2SiO_6$ system

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Abstract

A new bioglass-ceramics based on various content of the diopside [$CaMgSi_2O_6$]–fluorapatite [$Ca_5(PO_4)_3F$]–Ca-Tschermak's [$CaAl_2SiO_6$] system with minor additives of (Na_2O, B_2O_3 and TiO_2) were formulated.

The surface reactivity of the glass-ceramic specimens was studied in vitro in Kokubo's simulated body fluid (SBF). EDAX–SEM, and inductively coupled plasma (ICP) emission spectroscopy were used to characterize the glass-ceramic surfaces and the SBF compositional changes. Different bioactivity behaviour could be detected. Some samples showed a high reactivity with the (SBF) solution forming apatite rich layer on their surfaces as indicated from the EDAX–SEM and (ICP) data. However, other samples, which contain high percentage of Ca-Tschermak's component, i.e. rich in Al_2O_3, showed minimum presence or absence of apatite layer, which indicated that moderate or inert bioactive materials were also formed.

The prepared glass-ceramics had hardness, 6925–8055 MPa; thermal expansion coefficients in the 25–700 °C temperature range, 72×10^{-7} to 105×10^{-7} °C^{-1} and density values in the range, 2.78–2.94 g/cm^3.

Keywords: D. Glass-ceramics; Pyroxene ss; Fluorapatite; Properties; HA-forming; SBF solution

1. Introduction

Ceramics and glasses are frequently used as biomaterials for the repair of bone tissue. They are popular because of their generally biocompatibility and the ability of certain compositions to encourage the direct deposition of new bone tissue on their surface after implantation into established bone. This latter property is described as bioactivity or osteoconductivity [1]. Interestingly, the bioactivity of this ceramics can be studied in vitro, and the biological apatite layer can be formed when it is soaked in simulated body fluids [2].

A glass-ceramic processing route is an attractive method. It enables the component to form at high temperature in the glassy state, for example by lost wax die-casting, and then converted to the glass-ceramic by a controlled heat treatment [3]. For the in vitro study of the glass-ceramic A/W, Kokubo et al. [4] proposed in 1990 the Tris-buffered simulated body fluid (SBF) with an ion concentration nearly equal to that of human blood plasma. Since, unlike Tris-buffer alone, SBF contains calcium and phosphorous ions, it can be used to study the in vitro bioactivity of a wide variety of materials.

Natural bone and teeth are multiphase materials; their combination of properties probably can be simulated only by multiphase materials. Crystallization of glasses seems to be a very effective way to simulate hard tissues for those applications where elastic modulus mismatch and toughness are not important [5].

It should be mentioned that minerals capable of wide isomorphous substitution in their crystal structure and having the necessary physical and chemical characteristics, such as pyroxenes may form the basis for production of many melt casts and ceramic-like materials [6].

The system $Ca_5(PO_4)_3F$–$CaMgSi_2O_6$ provide fundamental knowledge for the development of new kinds of ceramics, glasses and bioglass-ceramics. It is claimed that the

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Table 1
The glass oxide constituents (mole%)

Glass no.	Oxides (mole%)						Calculated phase content (wt.%)			Heat-treatment (°C/h)	Phases developed
	SiO_2	Al_2O_3	MgO	CaO	P_2O_5	CaF_2	Di	Ca-Tsch.	FA		
G_1	40.76	–	20.1	33.32	4.36	1.46	75	–	25	720/5–925/10	Di + FA
G_1a	40.76	–	20.1	33.32	4.36	1.46	75	–	25	715/5–915/10	Di + FA
G_2a	42.0	1.34	20.05	31.98	3.47	1.16	75	5	20	705/5–925/10	Pyrox ss + FA
G_3a	46.67	6.63	20.05	26.65	–	–	75	25	–	750/5–970/10	Pyrox ss
G_4a	37.22	8.16	15.48	33.32	4.36	1.46	50	25	25	750/5–960/10	Pyrox.ss + FA + Geh

Di, diopside; Ca-Tsch., Ca-Tschermak's; FA, fluorapatite; Pyrox ss, pyroxene solid solution; Geh, gehlenite (a, additives: 2 g Na_2O, 0.5 g B_2O_3, 1 g TiO_2).

$Ca_5(PO_4)_3F$–$CaMgSi_2O_6$ glass-ceramic show a combination of high mechanical strength, a good chemical resistance and a good biocompatibility. Such materials are used as artificial implants in orthopedic surgery [7]. Ca-Tschermak's like diopside is a member of pyroxene group has good chemical and mechanical properties [6].

The aim of the present work was to determine the bioactivity behaviour by using (SBF) solution, hardness, thermal expansion and density properties of glass-ceramics based on various content of the stoichiometric compositions of diopside [$CaMgSi_2O_6$]–fluorapatite [$Ca_5(PO_4)_3F$]–Ca-Tschermak's [$CaAl_2SiO_6$] system with minor additions of Na_2O, B_2O_3 and TiO_2 to produce bioglass-ceramic suitable for medical applications.

2. Experimental methods

2.1. Glass composition and preparation

Table 1 shows the composition in mole percent of the glasses evaluated in this study. Glass batches were prepared from reagent grade powders of $CaCO_3$, SiO_2 (quartz), $MgCO_3$, $Al(OH)_3$, $NH_4H_2PO_4$, CaF_2, Na_2CO_3, H_3BO_3 and TiO_2. Glasses were melted in covered alumina crucibles in an electric furnace with SiC heating elements at 1450–1550 °C for 3 h. Melting was continued until clear homogeneous melt was obtained; this was achieved by swirling the melts several times at about 30-min intervals. After casting onto prior heated steel mold, the glasses were then properly annealed in muffle furnace at 650 °C for 1 h then cooled at 1 °C/min to room temperature to minimize the strain.

2.2. Differential thermal analysis

The thermal behaviour of the finely powdered (45–75 μm) glass samples was examined using a Netzsch Gerätebau GmbH Sleb Bestell-Nr. 348, 472 C. The powdered sample was heated in Pt-holder against another Pt-holder containing Al_2O_3 powder as a standard material. A uniform heating rate of 10 °C/min was adopted up to the appropriate temperature of the glasses. The results obtained were used as a guide for determining the heat-treatment temperatures applied to induce crystallization.

2.3. Preparation of glass-ceramic specimens

Samples (with dimensions 10 mm × 10 mm × 5 mm) were prepared from the as-cast glasses by a low speed diamond disc. These specimens were then heat-treated using double stage heat-treatment regimes. Crystallization was carried out at temperatures in the region of the different thermal analysis (DTA) exothermic peak determined for each glass. The glasses were first heated according to the DTA results at the endothermic peak temperatures for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h.

The glass-ceramic specimens were polished with α-Al_2O_3 powder and washed sequential with deionized water in an ultrasonic cleaner and then air-dried. These samples were chemically treated with 1.0 M HCl for 1 min, and then were removed from this solution, washed with ion-exchange deionized water and dried at room temperature.

2.4. Soaking in the SBF

Each specimen was soaked in 50 ml of Tris-buffered simulated body fluid (SBF) solution with ion concentrations and pH nearly equal to those of human blood plasma (Table 2) at 37 ± 0.5 °C, for 7, 14 and 21 days. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, and Na_2SO_4 into deionized water. The solution was buffered to pH 7.4 with Tris-(hydroxymethyl)-aminomethan [$(CH_2OH)_3$ CNH_3]and hydrochloric acid.

2.5. Surface analysis of specimens

The as-immersed crystalline samples were taken out after immersion in the (SBF) solution, then they washed with

Table 2
Ionic concentrations (mM) in the simulated body fluid (SBF) and human plasma

Occurrence	Ion concentration (mM)							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Human plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5

large amounts of deionized water and air dried. Surface analysis was conducted using the energy dispersive X-ray analysis (EDAX–SEM) using SEM Model Philips XL 30 attached with EDAX unit. The samples were coated with carbon. This technique was used to detect the elemental composition of the surfaces of all glass-ceramic materials before and after immersion in the SBF solution.

2.6. Elemental concentration analysis

Changes in the concentration of calcium, silicon, phosphorous and magnesium of the SBF solution due to soaking of the samples for 7, 14, and 21 days were measured using inductive coupled plasma (ICP) emission spectroscopy Model (J.Y. Jobian Yvon Horiba Ultima 2000).

2.7. X-ray powder diffraction analysis

Identification of crystal phases precipitating due to the course of crystallization was conducted by the X-ray diffraction patterns using a Philips type diffractometer (P.W. 1730) with Ni-filtered Cu Kα radiation.

2.8. Properties

2.8.1. Thermal expansion measurements

The coefficients of thermal expansion of the investigated glass-ceramics was carried out on 1.5–2.0 cm long rods using Linseis L76/1250 automatic recording multiplier Dilatometer with a heating rate of 5 °C/min. The linear thermal expansion coefficient was automatically calculated using the general equation:

$$\alpha = \frac{\Delta L}{L}\frac{1}{\Delta T}$$

where ΔL is the increase in length, ΔT is the temperature interval over which the sample is heated and L is the original length of the specimen.

2.8.2. Microhardness measurements

The microhardness of the investigated samples was measured by using Vicker's microhardness indenter (Shimadzu, Type-M, Japan). The eyepiece on the microscope of the apparatus allowed measurements with an estimated accuracy of ±0.5 μm for the indentation diagonals. Grinding and well polishing were necessary to obtain polished, smooth and flat parallel surfaces glass and glass-ceramic samples before indentation testing. At least six indentation readings were made and measured for each

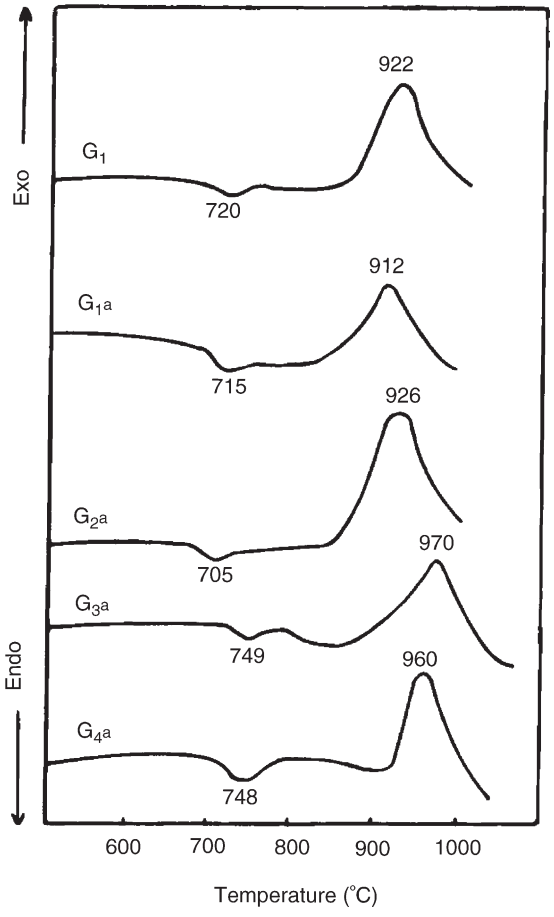

Fig. 1. DTA traces of the studied glasses.

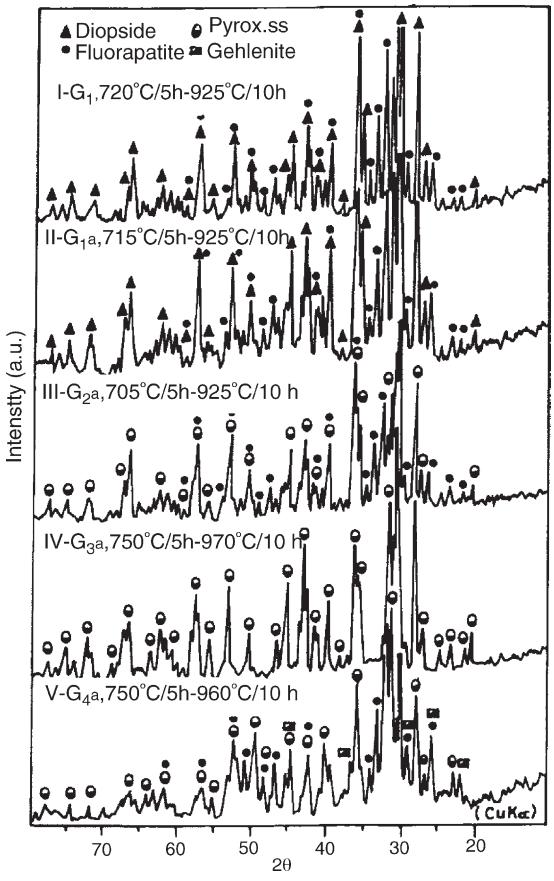

Fig. 2. XRD patterns of the studied glass-ceramic specimens.

sample. Testing was made by load 100 g and loading time was fixed for all glasses and crystalline samples (15 s). The measurements were carried out under normal atmospheric conditions. The Vicker's microhardness value was calculated from the following equation:

$$H_v = A\left(\frac{p}{d^2}\right) \text{kg/mm}^2$$

where A is a constant equal to 1854.5 takes into account the geometry of squared based diamond indenter with an angle 136° between the opposing faces, p is the applied load (g); and d is the average diagonal length (μm). The microhardness values are converted from kg/mm^2 to MPa by multiplying in a constant value 9.8 [8].

2.8.3. Density measurements

The density of the glass-ceramic specimens was determined at room temperature by using the Archimed's method, using xylene as immersion solution. The density (D) is calculated from the equation:

$$D = \frac{W}{(W-N)S}$$

where W is the weight of the sample in air, N is the weight of sample in xylene and S is the density of soaking solution (0.86 for xylene), to determine accurate density value, the arithmetic mean of three specimens of the same sample was calculated.

3. Results

The DTA curves of the studied glasses are presented in Fig. 1. Endothermic reactions at the temperature range of 705–749 °C were recorded. These endothermic peaks are to be attributed to the glass transition (T_g), at which the sample changes from solid to liquid like behaviour. Various exothermic effects at 912–970 °C indicating crystallization reaction in the glasses are also recorded.

The XRD analysis (Fig. 2) showed that the base glass composition G_1 and G_1a were crystallized to form diopside and fluorapatite phases. The addition of 5 wt.% of Ca-Tschermak's component at the expense of diopside component, i.e. G_2a, led to the development of pyroxene solid solution, and fluorapatite phases. On adding 25 wt.% Ca-Tschermak's component instead of fluorapatite, i.e. G_3a, pyroxene solid solution of diopsidic type was formed. While the combined presence of 25 wt.% Ca-Tschermak's, 25 wt.% fluorapatite and 50 wt.% diopside components, i.e. G_4a, resulted into the formation of pyroxene ss, fluorapatite and gehlenite phases (Table 1).

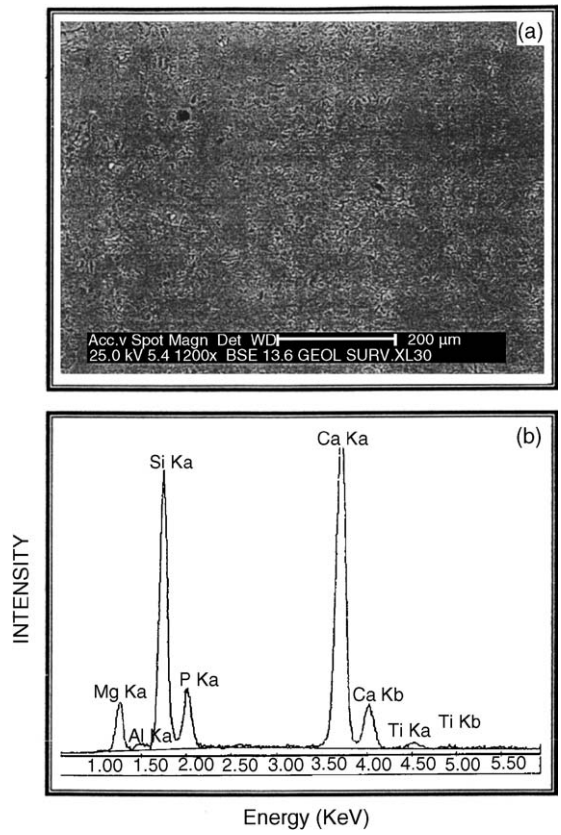

Fig. 3. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_1a before the immersion in the SBF solution.

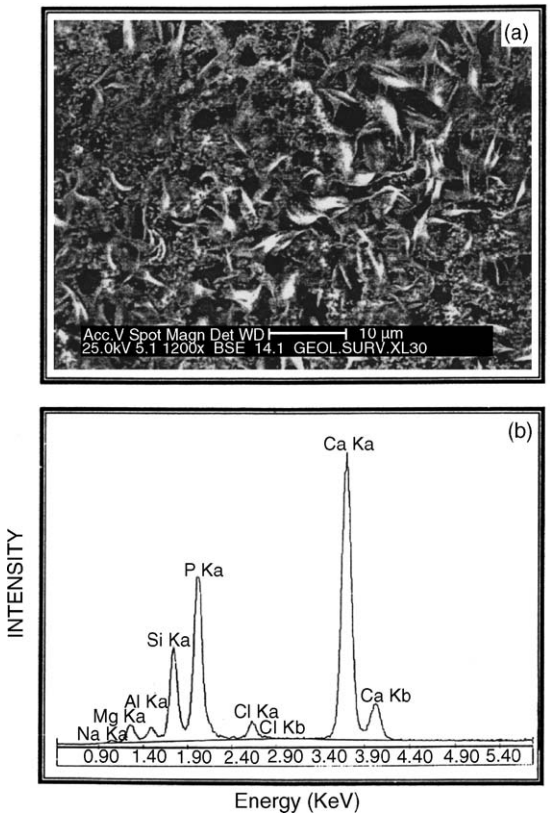

Fig. 4. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_1 after the immersion in the SBF solution for 21 days.

The study of the bioactivity test was carried out on the polished surfaces of the crystalline glass samples with and without minor additions of (B_2O_3 + Na_2O + TiO_2), e.g. G_1, G_1a, G_2a, G_3a and G_4a. SEM micrographs of the polished surfaces of the glass-ceramic specimens before and after chemical treatment with hydrochloric acid and SBF solutions are shown in Figs. 3a–8a. Fig. 3a showed the polished surface of sample G_1a without treatment by hydrochloric acid or (SBF) solution. Figs. 4a–8a showed the microstructure of the polished surfaces of the crystalline samples G_1–G_4a after immersion in the (SBF) solution. Fiber-like growths were observed on the surface of G_1 (Fig. 4a). Large cotton-like growths were present on the surface of G_1a (Fig. 5a), these cotton-like growths were due to the formation of the apatite layer also. The scanning electron micrograph (Fig. 6a) of the crystalline sample G_2a showed that the apatite layer grew around the edges of the crystallized phases. It was observed also that the surface of specimens G_3a and G_4a (Figs. 7a and 8a) were characterized by large amounts of pores and no evidence about the formation of apatite layer.

The (ICP) data are given in Table 3 and the following results could be outlined:

1. The changes of calcium and phosphorous concentrations in the SBF solutions after the immersion were found to be dependent on their contents in the parent glass compositions and the immersion time.
2. The silicon and magnesium concentrations in the SBF solution were gradually increased with the increase of the immersion time, and became more significant after 21 days test.

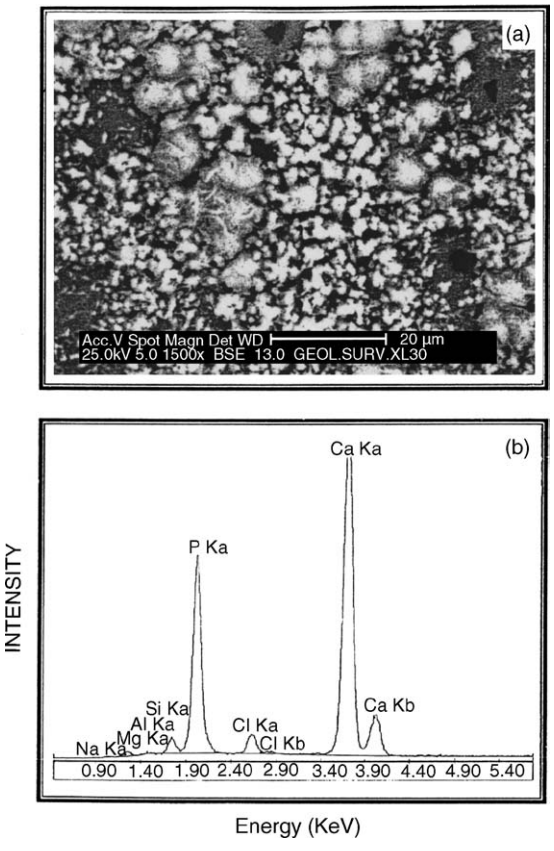

Fig. 5. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_1a after the immersion in the SBF solution for 21 days.

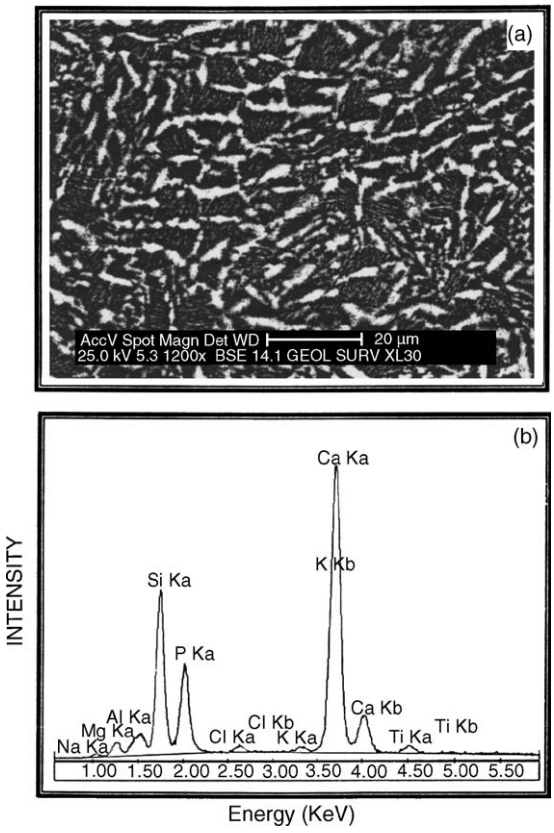

Fig. 6. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_2a after the immersion in the SBF solution for 21 days.

The data recorded in Table 3 revealed that the concentrations of calcium and phosphorous elements in the SBF solutions of samples G_1, G_1a, and G_2a were generally decreased while in case of G_3 and G_4 were increased with increasing the immersion time. There was another evidence to confirm the formation of apatite layer on the surfaces of the crystalline samples sought by using the energy dispersive X-ray analysis. Fig. 3b represented the EDAX spectra of the surface of the parent glass-ceramic G_1a (without immersion in SBF solution). It recorded the presence of Ca, Si, Mg, P, and minor amounts of Ti. The EDAX traces collected from the surfaces of the crystalline samples G_1–G_4a treated with 1.0 M (HCl) for one minute and SBF solution for 21 days were presented in Figs. 4b–8b.

The EDAX analysis of the surface of crystalline specimens G_1a and G_2a (Figs. 5b–6b) revealed that significant peaks of calcium and phosphorous were present. Figs. 6b–8b revealed that the intensity of silica peak increased while that for phosphorous peak was decreased.

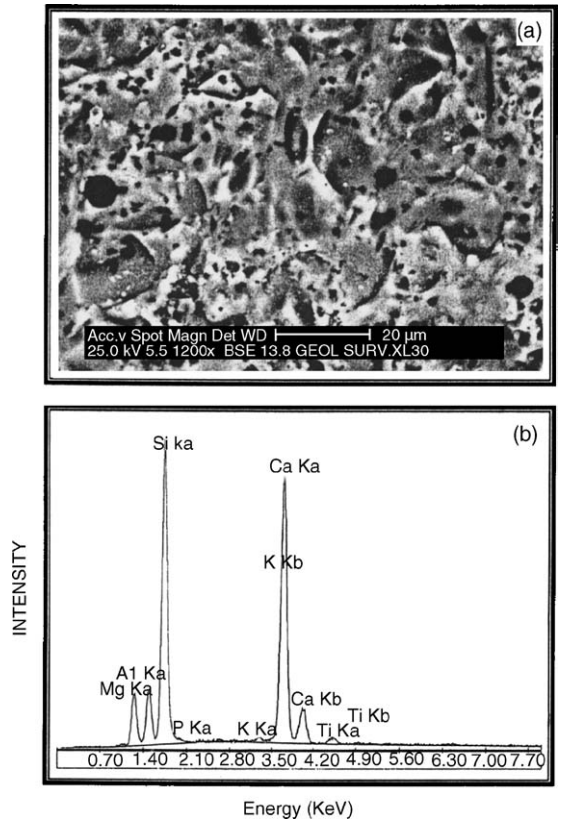

Fig. 7. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_3a after the immersion in the SBF solution for 21 days.

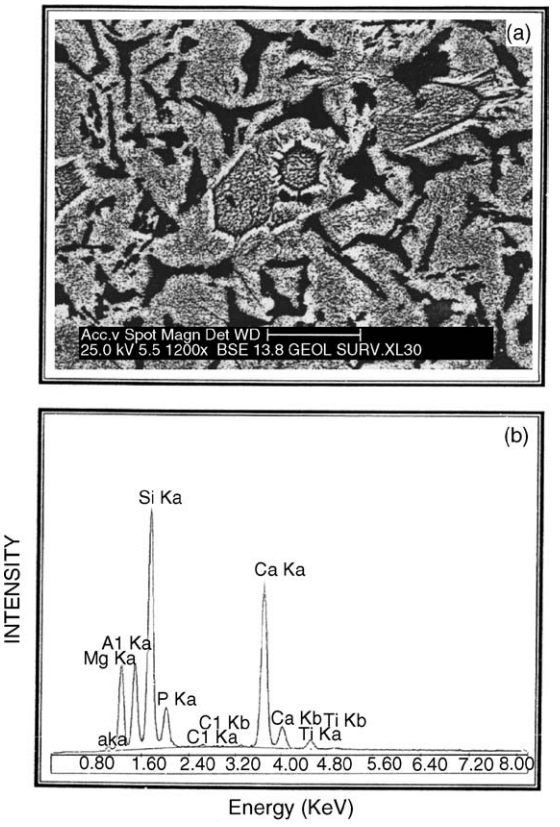

Fig. 8. (a) SEM micrograph and (b) EDAX spectrum of the surface of glass-ceramic specimen G_4a after the immersion in the SBF solution for 21 days.

There was no evidence for the formation of apatite layer on the surfaces of samples G_3a and G_4a.

Table 4 revealed that the investigated glass-ceramics containing diopside or pyroxene solid solution (of diopsidic type), gehlenite and fluorapatite phases had hardness 6925–8055 MPa, thermal expansion coefficients in the 25–700 °C temperature range were 72×10^{-7} to 105×10^{-7} °C^{-1} and characterized with variable bioactivity behaviour in the SBF solution. The density values of the studied glass-ceramics were in the range 2.78–2.94 g/cm^3

Table 3
Elemental concentrations in the SBF solution after the immersion of the glass-ceramic samples (i.e. G_1, G_1a, G_2a, G_3a, and G_4a) for 7, 14 and 21 days

Sample no.	Time (days)	Element concentrations (ppm)			
		Ca	P	Si	Mg
SBF (standard)		89.05	34.0	0.00	34.6
G_1	7	95	36.2	3.68	37.0
	14	93	31.26	5.03	38.3
	21	90.2	25.03	6.32	41.8
G_1a	7	97.8	29.2	14.5	40.8
	14	89.8	24.0	18.9	41.5
	21	85.3	19.37	31.0	54.9
G_2a	7	118	38.1	12.3	39.6
	14	117	32.3	13.3	43.6
	21	101	31.29	20.5	53.4
G_3a	7	92.3	34.24	1.39	35.4
	14	97.3	33.85	2.59	37.5
	21	127	34.54	6.3	46.3
G_4a	7	101	31.5	5.3	37.4
	14	106	34.7	9.36	39.5
	21	142.0	42.3	17.0	52.2

4. Discussion

The occurrence of the various phases formed in the present glasses was function of original composition of the glasses and the crystallization parameters used. There was no evidence for the formation of solid solution between diopside and fluorapatite phases formed in G_1 and this was in agreement with the results obtained by Tulyaganov [9].

At low Ca-Tschermak's/diopside ratios, i.e. G_2a and G_3a, pyroxene solid solution of diopsidic type was developed. It seemed, therefore, that the diopside phase, $CaMgSi_2O_6$, goes into solid solution with the Ca-Tschermak's, $CaAl_2SiO_6$, to form pyroxene solid solution ($CaMgSi_2O_6$–$CaAl_2SiO_6$). On increasing Ca-Tschermak's/diopside ratio up to 50%, i.e. G_4a, gehlenite phase (melilite) was developed in addition to fluorapatite and pyroxene ss phases, and these finding results are in a good agreement with those reported by Salama et al. [8], who determined the limit of the isomorphous substitution of Ca-Tschermak' component in

Table 4
Properties of the investigated glass-ceramic samples

Properties	G_1	G_1a	G_2a	G_3a	G_4a
Hardness (MPa)	6925	7085	7011	8013	8055
Density (g/cm^3)	2.93	2.94	2.92	2.78	2.87
Expansion coefficient, $\times 10^{-7}$ °C^{-1} (25–700 °C)	82	95	98	72	105

diopside as 25%. Schairer and Yoder [10] showed also that the maximum solubility of the Ca-Tschermak's pyroxene molecule ($CaAl_2SiO_6$) in diopside ($CaMgSi_2O_6$) is 20%, and that anorthite and melilite solid solutions are always present in the crystalline phases of the compositions greater than 20 wt.% of $CaAl_2SiO_6$.

Studies of carbonate containing hydroxy apatite (HCA) layer formed on the surface of bioactive materials have shown that reactions occur on the material side in five stages. These stages are faster for the highest level of bioactivity [11].

The results obtained by vitro study in the SBF solution of the five crystalline samples after polishing and etching with 1.0 M HCl for 1 min [12], concluded that each one showed different bioactivity behaviour in vitro test in the SBF solution. G_1 and G_1a glass-ceramic samples showed high reactivity with the SBF solution, forming a $CaO–P_2O_5$ rich layer on their surfaces [5], while G_2a showed regions on the surface at which calcium phosphate rich layer was formed. However, in other regions of the surface of G_2a only a minimum presence or absence of $CaO–P_2O_5$ layer was detected after the immersion in the SBF solution for 21 days. On the other hand, there is no $CaO–P_2O_5$ layer was detected on the surfaces of G_3a and G_4a. This indicated that inactive material was developed [1].

A quantitative analysis of the Ca, P, Si and Mg ions in the SBF solutions during and after in vitro test was very useful to complement the understanding of surface kinetic reactions in bioactive materials.

In the early stage of immersion of G_1, G_1a and G_2a (i.e. after 7 days), the concentrations of Ca, P, Si and Mg ions were increased in the SBF solutions. These results suggested that a relatively interaction between the SBF solution and the glass-ceramic samples occurred. This may be due to the release of alkali and alkaline earth ions, loss of soluble SiO_2 from the surface of the crystalline specimens to the SBF solutions and condensation and repolymerization of SiO_2-rich layer [11]. Calcium and phosphorous concentrations then fell in the SBF solutions with increasing the silicon and magnesium ion concentrations after 14 days duration, and this may be due to the formation of amorphous $CaO-P_2O_5$ layer. With increasing the silicon and magnesium, the subsequent rapid decrease in phosphorous and calcium ion concentrations in the SBF solution after 21 days immersion indicated that crystallization and growth of the $CaO–P_2O_5$ rich layer was occurred [13].

There was evidence to confirm the presence of apatite layer on the surfaces of crystalline specimens G_1, G_1a and G_2a with different magnitude, which was sought by using the EDAX/SEM technique. EDAX traces, which were represented in Figs. 4b, 5b and 6b of G_1, G_1a and G_2a, respectively, after 21 days immersion in the SBF solution, revealed that significant peaks for calcium and phosphorous with different ratios were detected due to the formation of apatite layer. SEM micrographs (Figs. 4a, 5a and 6a) confirmed also the presence of apatite layer on the surfaces of G_1, G_1a and G_2a, respectively.

On the other hand, the addition of ($B_2O_3 + Na_2O + TiO_2$) as minor additives showed a great positive effect on the bioactivity behaviour of the crystallized samples. It is clear that the bioactivity of the studied glass-ceramic with minor additives, e.g. G_1a was higher than that sample free of these additives, e.g. G_1 as indicated from the EDAX patterns of G_1 and G_1a (Figs. 4b and 5b), respectively. Fig. 5b revealed that short peak for silicon and long peak for phosphorous were developed in G_1a as compared with that of G_1 (Fig. 4b). This can be explained on the basis that these additives relieved the rigidity of the glass structure and increased the number of non-bridging oxygen bonds in the glassy phase that present in the crystallized glasses and this led to increase the bioactivity [14] of glass-ceramic material, G_1a.

Kobayashi et al. [15] revealed that the bioactivity of glass-ceramics depended mainly on the amount and composition of the residual glassy phase between the crystalline phases formed. However, during the heat-treatment process, the concentrations of alkali and alkaline ions decreased in glassy matrix and this led to hinder, the ion exchange between the alkali or alkaline ions from glass-ceramic samples and H^+ or H_3O^+ from the SBF solution [11], which could explain the low bioactivity of diopside–apatite glass-ceramics.

Therefore, the chemical etching of the crystalline samples with 1.0 M HCl for one minute led to an increase of the bioactivity of glass-ceramic materials as indicated by Roman et al. [12].

The modification of the base glass, G_1 (containing 75% diopside–25% fluorapatite) by increasing Ca-Tschermak's component at the expense of diopside or fluorapatite component was found to decrease the bioactivity, i.e. the development of aluminous pyroxene ss–($CaMgSi_2O_6$–$CaAl_2SiO_6$) and/or gehlenite-$Ca_2Al_2SiO_7$ phases were able to suppress the in vitro bioactivity of the studied glass-ceramics.

The ICP data are in good agreement with the EDAX spectra and SEM micrographs. It was found that the peak intensity of the EDAX patterns of the phosphorous ion was disappeared in case of G_3a sample while it was very short in case of G_4a (Figs. 7b and 8b).

The SEM micrographs showed that the surfaces of glass-ceramic samples G_3a (with 6.63 mole% Al_2O_3) and G_4a (with 8.16 mole% Al_2O_3) after the immersion for 21 days in the SBF solution were free of apatite layer (Figs. 7a and 8a). This was also supported by the ICP measurements, which showed that the concentrations of Calcium and Phosphorous elements in the SBF solution were increased with the immersion time. The reason for the absence of apatite rich layer on these surfaces may be attributed to the presence of large amounts of Al_2O_3 in the parent glass compositions, which acted as an inhibitor in the bioactivity mechanism [1,16]. Kokubo [17] showed that apatite-containing MgO–CaO–SiO_2–P_2O_5–Al_2O_3 glass-ceramics could not develop an HCA layer after 6 days in SBF solution if the residual glassy phase is chemically stable, i.e. rich in Al_2O_3.

The thermal expansion (α-values), microhardness and density properties revealed that the α-values and the microhardness of the crystalline samples increased with increasing Ca-Tschermak's/diopside ratios. The investigated glass-ceramics had hardness 6925–8055 MPa, thermal expansion coefficients in the 25–700 °C temperature range 72×10^{-7} to 105×10^{-7} °C^{-1}, and density values in the range 2.78–2.94 g/cm^3. However, the properties of the crystalline glasses were mainly attributed to different factors including the crystalline phases formed, residual glassy phase and the microstructures. The materials are most suitable for bone implants, dental crown and dental fillings as indicated by Tulyaganov and Aripova [7].

5. Conclusions

Bioactivity study of glass-ceramics based on various contents of the stoichiometric compositions of diopside–fluorapatite–Ca-Tschermak's system was investigated. Small changes in composition resulted in significant changes in the bioactivity behaviour in SBF solution.

The addition of (B_2O_3 + Na_2O + TiO_2) as minor additives showed a great positive effect on the bioactivity behaviour of the crystallized samples in the SBF solution after 7, 14 and 21 days. The bioactivity of the studied glass-ceramic with minor additives, e.g. G_1a was higher than that free of the additives. Bioactive glass-ceramics G_1, G_1a (free of Al_2O_3) and G_2a (with 1.34 mole% Al_2O_3) provided evidence for apatite deposition on their surfaces after the immersion for 21 days in the SBF solution as indicated from EDAX/SEM and ICP measurements.

The formation of apatite layer on G_3a and G_4a surfaces after the immersion for 21 days in the SBF solution could not be detected. This was attributed to the presence of large amounts of Al_2O_3 in the parent glass compositions, which acted as an inhibitor in the bioactivity mechanism.

References

[1] C.A. Miller, T. Kokubo, I.M. Reaney, P.V. Hatton, P.F. James, Formation of apatite layers on modified canasite glass ceramic in simulated body fluid, J. Biomed. Mater. Res. 59 (2002) 473–480.
[2] T. Kokubo, T. Kitsugi, T. Yamamuro, Ca, P rich layer formed on high strength bioactive glass ceramic A-W, J. Biomed. Mater. Res. 24 (1990) 331–343.
[3] A. Clifford, R.G. Hill, M.R. Towler, D.J. Wood, The crystallization of glasses from the ternary CaF_2–$CaAl_2Si_2O_8$–P_2O_5 system, J. Mater. Sci. 36 (2001) 3955–3961.
[4] T. Kokubo, H. Kushitani, S. Sakka, T. Kitsugi, T. Yamamuro, Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramics A-W, J. Biomed. Mater. Res. 24 (1990) 721–734.
[5] A.J. Salinas, J. Roman, M. Vallet-Regi, J.M. Oliveira, R.N. Correia, M.H. Fernandes, In vitro bioactivity of glass and glass ceramics of the $3CaO{\cdot}P_2O_5$–$CaO{\cdot}SiO_2$–$CaO{\cdot}MgO{\cdot}2SiO_2$ system, Biomaterials 21 (2000) 251–257.
[6] W.A. Deer, R.A. Howie, J. Zussman, An Introduction to the Rock Forming Minerals, second ELBS ed., Printing Press Ltd., Hong Kong, 1992.
[7] D.U. Tulyaganov, M. Aripova, Bioactive glass-ceramic containing anorthite and diopside crystals, XVI Proc. Int. Congr. Glass, Bol. Soc. ESP Ceram. VID, 31-C, 5 (1992) 227–232.
[8] S.N. Salama, H. Darwish, H.A. Abo-Mosallam, Crystallization and properties of glasses based on diopside–Ca-Tschermak's–fluorapatite system, J. Eur. Ceram. Soc. 25 (2005) 1133–1142.
[9] D.U. Tulyaganov, Phase separation and devitrification in the fluorapatite–diopside system, in: Proceedings of the XIX Int. Congr. Glass, vol. 2, Extended abstract, Edinburgh, Scotland, 1–6 July, 2001, p. 198.
[10] J.F. Schairer, H.S. Yoder Jr., Crystal and liquid trends in simplified alkali basalts, YearBook, vol. 63, 1964, pp. 64–74.
[11] L.L. Hench, G. La Torre, Reaction kinetics of bioactive ceramics, Part IV: Effect of glass and solution composition, in: T. Yamamuro, T. Kokubo, T. Nakamura (Eds.), Bioceramics, 5, Kobonshi Kankokai, Inc, Kyoto, Japan, 1992, pp. 67–74.
[12] J. Roman, A.J. Salinas, M. Vallet-Regi, J.M. Oliveira, R.N. Correia, M.H. Fernandes, Role of acid attack in the in vitro bioactivity of glass-ceramic of the $3CaO{\cdot}P_2O_5$–$CaO{\cdot}SiO_2$–$CaO{\cdot}MgO{\cdot}2SiO_2$ system, Biomaterials 22 (2001) 2013–2019.
[13] J.M. Oliveira, R.N. Correia, M.H. Fernandes, Effects of Si speciation on the in vitro bioactivity of glasses, Biomaterials 23 (2002) 371–379.
[14] K.H. Karlsson, H.O. Ylanen, Porous bone implants, in: P. Vincenzini (Ed.), Materials in Clinical Applications, Advances in Science and Technology, 28, 9th Cimtec-World Forum on New Materials, Florence, Italy, 33, 1998.
[15] T. Kobayashi, K. Okada, T. Kuroda, K. Sato, Osteogenic cell cytotoxicity and biomechanical strength of the new ceramic diopside, J. Biomed. Mater. Res. 37 (1997) 100–107.
[16] L.L. Hench, J. Wilson, Surface-active biomaterials, Science 226 (1984) 630–636.
[17] T. Kokubo, Surface chemistry of bioactive glass-ceramics, J. Non-Cryst. Solids 120 (1990) 38–51.