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## The effect of aqueous media on the mechanical properties of fluorapatite–mullite glass–ceramics

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### ABSTRACT

**Objectives.** To verify the effects of alternating thermal changes in aqueous media and chemical composition on mechanical properties of apatite–mullite glass–ceramics and to investigate concentration of ions eluted from glass–ceramics in aqueous media.

**Materials and methods.** The glass compositions were from  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--CaO--TiO}_2\text{--BaO--ZrO}_2\text{--CaF}_2$  system. Glass–ceramics were prepared by heat-treating at  $1100^\circ\text{C}$  for 3 h samples alternately immersed in water at 5 and  $60^\circ\text{C}$ . The 3-point bending strength ( $n=10$ ) were determined using  $3 \times 4 \times 25$  mm/bar and a universal testing machine, at a cross-head speed of 0.1 mm/min. Vickers micro hardness were evaluated by applying a total of 15–20 indentations under a 100 g load for 30 s. Concentrations of ions eluted from glass–ceramics immersed in  $60 \pm 5^\circ\text{C}$  double distilled water were determined by ion chromatography. The toxicity of glass–ceramics was assessed by seeding the osteosarcoma cells (MG63) on powder for different days and their cell proliferation assessment was investigated by MTT assay. The data were analyzed using one way analysis of variance and the means were compared by Tukey's test (5% significance level).

**Results.** The highest flexural strength and hardness values after thermal changes belonged to  $\text{TiO}_2$  and  $\text{ZrO}_2$  containing glass–ceramics which contained lower amount of released ions. BaO containing glass–ceramic and sample with extra amount of silica showed the highest amount of reduction in their mechanical strength values. These additives enhanced the concentration of eluted ions in aqueous media. MTT results showed that glass–ceramics were almost equivalent concerning their in-vitro biological behavior.

**Significance.** Thermal changes and chemical compositions had significant effects on flexural strength and Vickers micro-hardness values.

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## 1. Introduction

The growing trend for dental restorative materials has pushed on to the development of novel glass–ceramic systems [1–3]. Glass–ceramics are composed of one or more crystalline phases which are surrounded by a glassy matrix. Heat-treatment process of the base glass which contains controlled crystallization and growth steps is one of the conventional methods in preparation and manufacturing of glass–ceramics [4]. These materials have advantages over other bioceramics since their mechanical and biological properties are easily adjustable by using different amount of additives [3–5]. The anti-bacterial effect of  $F^-$  ions and the presence of needle-like fluorapatite crystals in natural bone and teeth make fluorapatite containing glass–ceramics promising candidates for medical and dental applications [6–9]. Glass–ceramics based on interlocking microstructures of apatite and mullite crystals have previously been developed for dental restorations [10–14]. These glass–ceramics contain dispersed fluorapatite ( $Ca_{10}(PO_4)_6F_2$ ) and mullite crystals ( $3Al_2O_3 \cdot 2SiO_2$ ) in a glassy matrix [10–14]. Small crystals of fluorapatite, in these materials, result in biocompatibility and very special optical properties such as translucency and opalescence whilst mullite crystals induce adequate mechanical properties [11,13]. Microstructure and chemical characteristic of glass–ceramic materials, chemical nature and temperature of the surrounding environment and duration of exposure to this environment are some factors which can manipulate the mechanical performance and chemical durability of dental glass–ceramics [15–17]. Rapid and cyclic thermal changes in the oral cavity, which can exert considerable thermal stresses on the restorations solely or in the presence of the applied load of chewing process, are some of the other crucial issues which have unfavorable effects on mechanical properties of these materials [16–19]. These thermal stresses can be simulated by thermo-cycling process which is based on alternating temperature changes in aqueous media [18]. In a separate study, we focused on the performance of minor glass ingredients such as  $TiO_2$ ,  $ZrO_2$ ,  $BaO$  and additional amount of silica in points of crystallization behavior, microstructure and mechanical properties of an apatite–mullite based glass–ceramic system [20]. Our results showed that small amounts of the above mentioned additives changed the microstructure and mechanical properties of the base glass–ceramic system in different ways [20]. Despite the numerous studies about the effect of aqueous and acidic media on mechanical properties of silicate glasses, to our knowledge few studies have investigated the effect of alternative thermal changes on flexural strength and hardness variations in dental glass–ceramics [17–19]. Such information is of practical importance to manufacture and application of apatite–mullite glass–ceramics in dentistry and other biomedical applications and can lead to better prediction of the future clinical behaviors of these materials [17–19]. Therefore, the objective of this study is to verify the effect of thermo-cycling process duration on the strength and microhardness properties of the apatite–mullite glass–ceramics, concerning their different microstructures and chemical compositions.

## 2. Materials and methods

### 2.1. Specimen preparation

The raw materials used to produce the glass–ceramic samples are shown in Table 1. 5 groups of glass–ceramics coded as G, GS, GZ, GB and GT with the batch formulations shown in Table 2 were prepared according to the procedure completely described in [20]. Briefly, thoroughly mixed batches were melted at  $1550^\circ C$  for 2 h. The resulted molten glasses were cast into a pre-heated steel mold and were cooled naturally to room temperature. Flexural strength and micro-hardness samples were prepared by cutting rectangular bars from as-mentioned glass blocks. All samples were annealed at  $500^\circ C$  for 4 h. Based on the previously reported DTA and XRD results [20], obtained glass samples were first heat treated to  $650^\circ C$  at a heating rate of  $5^\circ C/min$  for 3 h, and then to  $1100^\circ C$  at a heating rate of  $10^\circ C/min$  for another 3 h and finally furnace cooled to room temperature. Microhardness samples were continually ground 5–10 min with abrasive grade SiC papers ranging from 60 grit to 1500 grit sizes and finally polished 5 min with  $0.2\ \mu m$  diamond paste until all scratches were removed. Specimens were washed in an ultrasonic bath after each step of grinding.

### 2.2. Thermocycling

Before testing, the prepared specimens for flexural strength and hardness analysis were alternately immersed in double distilled de-ionized water at  $5 \pm 5^\circ C$  for 20 s, ambient temperature for 20 s and finally double distilled de-ionized water at  $60 \pm 5^\circ C$  for 20 s. Flexural strength and microhardness values of each composition were assessed after specified number of cycles (dry state or 0 cycle, 3500, 7500, 18,000 and 24,000 cycles).

### 2.3. Flexural strength and micro-hardness assessments

The 3-point bending strength of specimens were determined using rectangular bars ( $3 \times 4 \times 25\ mm$ ) [20] and a universal testing machine (SANTAM-20, Iran-Tehran), at a cross-head speed

**Table 1 – The chemical composition of different glasses [20].**

Sample code	G	GS	GZ	GB	GT
$SiO_2$	21.03	31.27	20.49	20.49	20.49
$Al_2O_3$	35.06	30.51	34.15	34.15	34.15
CaO	8.60	7.47	8.36	8.36	8.36
CaF <sub>2</sub>	18.93	16.47	18.44	18.44	18.44
$P_2O_5$	16.38	14.26	15.96	15.96	15.96
$TiO_2$	–	–	–	–	2.56
BaO	–	–	–	2.56	–
$ZrO_2$	–	–	2.56	–	–

**Table 2 – Technical information (code and company) of raw materials used to produce the glass–ceramic particles.**

Raw material	SiO <sub>2</sub>	Al(OH) <sub>3</sub>	CaF <sub>2</sub>	Ca(CO) <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Ba(CO) <sub>3</sub>	ZrO <sub>2</sub>
Code	–	239186	378801	481807	79609	14021	237108	204994
Company	Industrial SiO <sub>2</sub> (purified)	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich

of 0.1 mm/min. Flexural strength values for glass–ceramics samples were calculated using the following relationship [20]:

$$FS = \frac{3PL}{2WD^2} \quad (1)$$

where FS is flexural strength (MPa); P is failure load (N); L is specimen length (mm); W is specimen width (mm) and D is specimen height (mm). In order to evaluate the Vickers surface microhardness of glass and glass–ceramic samples total of 15–20 indentations were made under a 100 g load applied for 30 s on the top surface of each specimen. The reported hardness values were an average of these readings.

#### 2.4. Ion elution and MTT assay

In order to investigate the effect of 60 °C water exposure on leaching of some ions in glass–ceramic samples which may imply their chemical resistance, concentrations of PO<sub>4</sub><sup>3-</sup>, Ca<sup>2+</sup> and F<sup>-</sup> ions eluted from glass–ceramic samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ES 700-VarianBV, Australia2007) after 1, 2 and 4 weeks of immersion in 60 ± 5 °C double distilled de-ionized water. Briefly, for this purpose, calibration was performed using titrisol (MERC) stock standard solutions. After immersion in 60 °C water (for 1, 2 and 4 weeks), glass–ceramic samples were pulverized and sieved to have a uniform particle size of about 200 μm in all samples. To measure the amounts of ions eluted from the glass–ceramic samples, 10 mg of each sample powder was dispersed in about 25 ml of the buffer solution and soaked for 1 week. The measurement was repeated about seven times for each ion, to ensure the reproducibility of the results.

The toxicity of glass–ceramic samples was assessed by seeding the osteosarcoma cells (MG63) on powder extracts for 7, 14 and 28 days. The proliferation and differentiation rates of the osteoblast-like cells were evaluated using extracted powders prepared according to ISO 1993-5 procedure [21]. 0.1 g of powder samples with different compositions were incubated in 1 ml of culture medium. At the end of 7, 14 and 28 days, the mediums were collected for use in different cellular assays. Pure culture medium kept under similar conditions was used as a negative control sample. The proliferation rate of the osteoblast-like cells next to different powder extracts was determined by conducting the 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay. This test is based on the fact that active cells convert the yellowish MTT to an insoluble purple formazan crystal properties [21]. The data (flexural values, microhardness, ions concentration and cell proliferation) were analyzed using one way analysis of variance (ANOVA) and the means were compared by Tukey's test

**Table 3 – The variation in flexural strength values (MPa) of glass–ceramic samples during thermo-cycling process.**

Sample code	Numbers of thermal-cycles	Flexural strength (SD) (MPa)
G	0	173 (22) a
G	3500	168 (10)a
G	7500	159 (10) <sup>#</sup> b
G	12,000	140 (12)b
G	18,000	118 (13)d
G	24,000	121 (13)d
GS	0	180 (38)f
GS	3500	170 (13)f
GS	7500	132 (21) <sup>#</sup> g
GS	12,000	138 (12)g
GS	18,000	118 (11)c
GS	24,000	110 (15)c
GZ	0	213 (38)e
GZ	3500	204 (22)e
GZ	7500	198 (18)e
GZ	12,000	176 (16) <sup>#</sup> f
GZ	18,000	160 (15)f
GZ	24,000	164 (10)f
GB	0	247 (29)h
GB	3500	252 (11)h
GB	7500	240 (18)h
GB	12,000	232 (14)h
GB	18,000	193 (10) <sup>#</sup>
GB	24,000	164 (18)
GT	0	235 (27)i
GT	3500	240 (11)i
GT	7500	233 (18)i
GT	12,000	220 (13)i
GT	18,000	194 (15)i
GT	24,000	183 (15) <sup>#</sup>

\* The numbers in () are standard deviations.

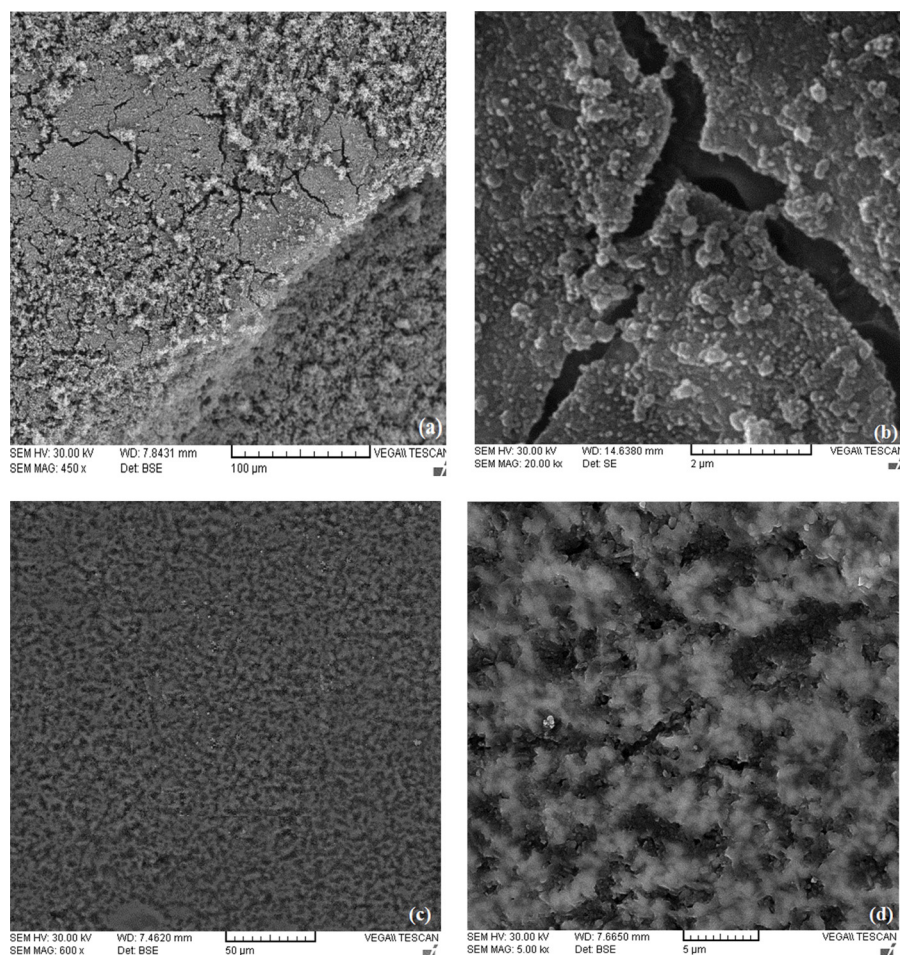
<sup>#</sup> Denotes the number of cycles at which first significant decline in flexural strength values of each composition happened ( $p < 0.05$ ). a–i Indicate that there are no significant differences between values marked with similar letters ( $p < 0.05$ ).

(5% significance level,  $p > 0.05$  is for no significant difference and  $p < 0.05$  is for significant difference).

### 3. Results

#### 3.1. Mechanical properties

Table 3 depicts the flexural strength of glass–ceramic samples at specified number of thermal-cycles. As indicated in this table, flexural strength values declined with different rates after thermal process. The number of cycles at which mechanical strength of different glass–ceramic



**Fig. 1** – Surfaces of glass–ceramic compositions at initial stage of thermocycling process ((a) and (b) GS sample at lower and higher resolution, respectively, (c) and (d) GT sample sample at lower and higher resolution, respectively).

compositions experienced first significant decline and the amount of ultimate loss were two crucial factors which were distinctive in prepared glass–ceramic compositions. The results of Table 3 indicated that mechanical properties of G, GS and GZ glass–ceramic compositions decreased rapidly at initial stages of thermo-cycling process while strength of GB started to decline at higher number of cycles and flexural strength of GT decreased at the end of thermo-cycling process. The results of Table 3 also implied that at the end of the cycling procedure, there were higher amounts of reduction in flexural strength values of GS and GB compositions, while GZ and GT glass–ceramic compositions experienced lower percentage of decline in their flexural strength values (about 39%, 23%, 34% and 22%, respectively). Finally, G sample had moderate percentage of changes in its mechanical strength (about 29%). Fig. 1(a–d) represents the surface of the GS and

GT glass–ceramics respectively, at initial stages of the thermo-cycling process. It can be seen that, compared to surface of GT, some cracks has been extended on the surfaces of GS during this process. The results of the Vickers microhardness test for different glass and glass–ceramic compositions are given in Table 4. Microhardness of the glasses and glass–ceramics were found to lie in the range of 180–247 and 550–990 Vickers, respectively. As the results of Table 4 pointed out there were remarkable variations in the hardness values of glasses and glass–ceramics with the addition of small amounts of oxides. GS glass composition presented statistically the highest mean microhardness value among investigated glass compositions while GB glass showed the lowest one ( $p < 0.05$ ). The observed trend was different in glass–ceramic samples. GZ and GT glass–ceramic compositions presented statistically higher mean microhardness values than that of the other

**Table 4** – Mean Vickers microhardness values of glasses and glass–ceramics before exerting thermal changes.

Sample code	G	GS	GZ	GB	GT
Vickers micro-hardness of glasses (SD)	203 (84)♣	331 (120)	217 (61)♣	150 (59)	219 (100)♣
Vickers micro-hardness of glass–ceramics (SD)	669 (84)♦	676 (157)♦	880 (95)*	560 (75)	995 (110)*

♣, ♦ and \* Denote that there is no significant difference between values marked with similar symbols ( $p < 0.05$ ).



**Table 5 – The variation in Mean Vickers microhardness values of glass–ceramic samples during thermo-cycling process.**

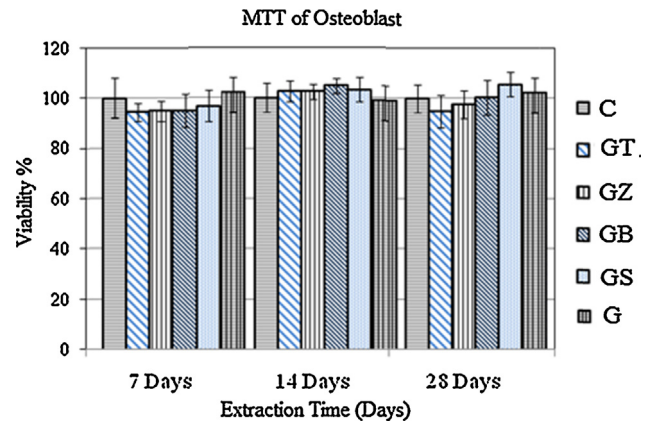
Sample code	Numbers of thermal-cycles	Vickers microhardness (SD) (HV)
G	3500	648 (96) <sup>a</sup>
G	7500	600 (65) <sup>a</sup>
G	12,000	458 (70) <sup>#,b</sup>
G	18,000	487 (60) <sup>b</sup>
G	24,000	460 (60) <sup>b</sup>
GS	3500	665 (49)
GS	7500	500 (70) <sup>#,c</sup>
GS	12,000	560 (69) <sup>c</sup>
GS	18,000	433 (80)
GS	24,000	398 (92)
GZ	3500	845 (52) <sup>d</sup>
GZ	7500	883 (88) <sup>d</sup>
GZ	12,000	846 (70) <sup>d</sup>
GZ	18,000	720 (90) <sup>#</sup>
GZ	24,000	630 (70)
GB	3500	517 (69) <sup>e</sup>
GB	7500	552 (42) <sup>e</sup>
GB	12,000	411 (62) <sup>#,f</sup>
GB	18,000	438 (70) <sup>f</sup>
GB	24,000	385 (67)
GT	3500	965 (11) <sup>g</sup>
GT	7500	942 (81) <sup>g</sup>
GT	12,000	900 (76) <sup>g</sup>
GT	18,000	842 (93) <sup>g</sup>
GT	24,000	780 (48) <sup>#</sup>

<sup>a–g</sup> Indicate that there are no significant differences between values marked with similar letters ( $p < 0.05$ ).  
<sup>#</sup> Denotes the number of cycles at which first significant decline in mean microhardness values of each composition happened ( $p < 0.05$ ).

glass–ceramic samples ( $p < 0.05$ ). Although it may sound that GB glass–ceramic presented the lowest microhardness values, closer look shows that the microhardness values of G, GS and GB increased with the same rate after heat treatment. Table 5 represents the variation of the Vickers microhardness values as a result of thermal-cycling process for different glass–ceramic compositions. The microhardness values of glass–ceramic samples decreased after thermo-cycling process with different trends. The highest amount of reduction was observed in glass–ceramic samples GS, GB and G (46%, 31% and 31%, respectively). GZ and GT samples showed moderate changes in their hardness values (25% and 21%, respectively).

### 3.2. Ion release concentrations and MTT results

The mass concentration of  $F^-$ ,  $PO_4^{3-}$  and  $Ca^{2+}$  ions eluted from different glass–ceramic compositions after immersion in hot water for 1, 2 and 4 weeks are summarized in Table 6. Based on these results the mass concentration of  $F^-$  ions released from G, GS and GB samples increased over time. The amount of eluted phosphorous ions ( $PO_4^{3-}$ ) in all compositions decreased significantly during time while the concentration of released  $Ca^{2+}$  did not change ( $p < 0.05$ ). GZ and GT compositions had the lowest amount of washed out ions during exposure to hot water ( $p < 0.05$ ). Fig. 2 represents the results of



**Fig. 2 – The osteoblast-like cell viability results for various extracted powder samples.**

the percentage cell viability for various powder extracts. The MTT assay was done at least five times for each glass–ceramic sample. The error bars in Fig. 2 depict to standard deviation of the viability percent of glass–ceramic samples after different times of extraction. MTT results (Fig. 2) showed that glass–ceramic samples were almost equivalent concerning their in vitro biological behavior.

## 4. Discussions

The rapid decline in flexural strength values of G, GS and GZ glass–ceramic compositions at the initial stages of the thermo-cycling process can be partly attributed to higher amounts of residual glassy phase in these samples [14,20]. Previously reported DTA results [20] indicated that higher viscosity of the aforementioned glasses led to the crystallization at relatively higher temperatures. Late onset of crystallization in these glasses resulted in higher amounts of residual glassy phase at the end of the heat-treatment process at 1100°C [20]. More content of remaining glassy phase and thermal expansion coefficient mismatches between glassy and crystalline phases led to the nucleation and growth of more cracks in the microstructure of these samples during thermo-cycling process. These items could reduce the mechanical strength of the above mentioned glass–ceramics more rapidly at the initial stages of thermo-cycling process [20,22–24]. The SEM micrographs of the samples (Fig. 1a and b) can support the above-mentioned results. Reaction with water and hydrolytic effect at the surface of the samples could also cause these microcracks and observed reduction in flexural strength values [25]. Although the mechanical strength of GB glass–ceramics started to decline at greater number of cycles, this sample as well as GS glass–ceramic composition presented the highest amount of reduction in flexural strength values ( $p < 0.05$ ). Conversely, GZ and GT had the lowest amount of reduction in their mechanical strength at the end of thermo-cycle process ( $p < 0.05$ ). Modification in the chemical structures of glass–ceramic samples in water based environment and applied thermal variations were the main reasons why the mentioned changes occurred [23–25]. Hardness is an important parameter, since it can be an indicator

**Table 6 – The concentration of released ions over time of immersion in hot water.**

Sample name	G	GS	GZ	GB	GT
Concentration of the released F <sup>-</sup> ion after 1 week of immersion (ppm) (SD)	30 (4) <sup>a,▼</sup>	32 (2) <sup>▼</sup>	8 (2)	22 (3)	12 (3)#
Concentration of the released F <sup>-</sup> ion after 2 weeks of immersion (ppm) (SD)	39 (2)*	42 (2)*	13 (2)#	30 (3)	19 (5)#
Concentration of the released F <sup>-</sup> ion after 4 weeks of immersion (ppm) (SD)	51 (8)	64 (5)	8 (3)#	43 (4)	17 (6)#
Concentration of the released PO <sub>4</sub> <sup>3-</sup> ion after 1 week of immersion (ppm) (SD)	72 (6)	60 (5)◆	17 (5)□	53 (6)◆,◇	2 (2)
Concentration of the released PO <sub>4</sub> <sup>3-</sup> ion after 2 weeks of immersion (ppm) (SD)	93 (7)	75 (8)	15 (4)□	57 (6)◇	7 (2)∞
Concentration of the released PO <sub>4</sub> <sup>3-</sup> ion after 4 weeks of immersion (ppm) (SD)	30 (8)	52 (7)	4 (1)	40 (5)	3 (1)∞
Concentration of the released Ca <sup>2+</sup> ion after 1 week of immersion (ppm) (SD)	17 (5)■	15 (3)■	7 (1)	10 (4)■	3 (3)Δ
Concentration of the released Ca <sup>2+</sup> ion after 2 weeks of immersion (ppm) (SD)	14 (4)■	13 (3)■	2 (1)■	12 (3)■	6 (3)Δ
Concentration of the released Ca <sup>2+</sup> ion after 4 weeks of immersion (ppm) (SD)	12 (5)■	11 (3)	0 (0.1)■	12 (7)■	2 (1)Δ

\*, #, ∞, Δ, and ■ Denote that there is no significant difference between values marked with similar symbols ( $p < 0.05$ ).

<sup>a</sup> The numbers in () are standard deviations.

of the wear resistance [14]. The reported values of Vickers micro hardness of glass and glass–ceramic samples are the average of at least 15 measurements on the surface of each sample. The micro-hardness values of glass–ceramic samples are the average micro-hardness values of their constitutive crystalline and glassy phases (phase). As a result, the amount and type of crystalline phase (phases), microstructural properties of these phases like their morphology and distribution in the glassy phase and the type or amount of glassy phase have direct effect on final micro-hardness values of glass–ceramic samples [18]. Accordingly, observed changes in the microhardness values of glass and glass–ceramic samples as a result of different oxide additives could be explained as following: Increasing the amounts of SiO<sub>2</sub> caused the Vickers microhardness values increased considerably among the glass series but moderately among the glass–ceramics. The previous results of XRD and DTA [20] showed that different additive oxides could affect the crystallization behavior of the base glass in different ways. For instance, GS glass sample had higher crystallization temperature compare to other glass composition. These results [20] implied that addition of SiO<sub>2</sub> could increase the amount of bridging oxygens, therefore, structural bonds would be stronger and resultant glass would have more integrity [20,26–29]. So as Table 4 shows, GS sample with excess amount of SiO<sub>2</sub> and higher amount of bridging oxygens had the highest hardness value among glass series. Such a glass composition should also be more resistant to crystallization; Thus, it would contain lower amounts of crystalline phases and show lower improvement in the micro hardness properties after heat treatment and crystallization [26–29]. Accordingly, as XRD results showed [20] higher amount of SiO<sub>2</sub> could postpone or prevent the crystallization of mullite, after thermal heat treatment at 1100 °C. As a result, after 3 h thermal heat-treatment at 1100 °C fluorapatite was the main crystalline phase in this sample. So lower amount of mullite crystalline phase which had higher hardness value compare to fluorapatite, resulted in lower improvement of hardness after thermal heat treatment in glass–ceramic series.

The observed increase in micro hardness values of the glasses with the addition of ZrO<sub>2</sub> and TiO<sub>2</sub> is thought to be the result of high ionic field strength of Zr<sup>4+</sup> and Ti<sup>2+</sup> ions [27–30]. It has been also stated that Zr<sup>4+</sup> can strengthen the silicate network via forming the covalent Zr–O–Si bridges; hereby it improves the hardness of glass samples [30]. Previously reported elongated and rod shaped morphology of crystalline phases in GZ and GT glass–ceramics [20], higher amount

of crystalline phases and their distribution [20] and totally higher hardness values of base glasses lead to the higher Vickers microhardness values of GZ and GT glass–ceramics. On the other hand, addition of BaO to the base glass had led to 34% reduction of Vickers micro hardness in the studied glass samples. It could be due to the interrupting of the glass network by BaO addition based on the previous DTA and XRD results [20]. It is also well known that the micro-hardness is related to the ionic field strength of the glass constituents, meaning that lower field strength leads to lower microhardness values [31,32]. Ba<sup>2+</sup> ion has a large ion radius and so has the less ionic field strength comparing with the other glass constituents. Therefore, the lowest microhardness values of the glass and glass–ceramic GB among samples would be reasonable [31,32]. The microhardness values of glass–ceramic samples decreased after thermo-cycling process. The observed changes in microhardness values of glass–ceramic samples after thermal procedures in aqueous media were consistent with their chemical stability variations after immersion in hot water over time. Increasing the time of immersion in 60 °C water, increased the concentration of F<sup>-</sup> ion eluted from GS glass–ceramic composition. As Fig. 1(a) demonstrated, this reduction in chemical stability could possibly attributed to high amounts of surface cracks in the residual glassy phase in GS composition. The drop in hardness value of GS glass–ceramic sample after thermo-cycling process could be the result of observed chemical stability reduction [33]. The concentration of ions released from ZrO<sub>2</sub> and TiO<sub>2</sub> including glass–ceramic samples did not change significantly over time of immersion. Improved chemical resistance and consequential durable hardness values of GZ and GT glass–ceramics compositions could be due to the higher amount of mullite phase and higher amount of crystalline phases, respectively [20,33]. The reduction of the water stability and hardness values was also observed in G and GB glass–ceramic compositions. These could be explained by less cross-linked glass network and easier diffusion of ions [31,32]. The MTT results indicate that all of the glass–ceramic samples are biocompatible and the additive oxides and extra amount of SiO<sub>2</sub> don not led to the toxicity after 28 days cell proliferation.

## 5. Conclusion

Flexural strength and hardness values of apatite–mullite glass–ceramic samples including distinctive amounts of TiO<sub>2</sub>,

ZrO<sub>2</sub>, BaO and extra amounts of SiO<sub>2</sub> changed differently after thermo-cycling process. While after thermal changes, mechanical properties values remained almost un-changed in glass-ceramic samples containing small amounts of TiO<sub>2</sub> and ZrO<sub>2</sub>, these values experienced the highest amounts of reduction with the addition of BaO and extra amounts of SiO<sub>2</sub>. After immersion in hot water, the concentration of Ca<sup>2+</sup> and F<sup>-</sup> ions released from samples with BaO or excess amounts of SiO<sub>2</sub> were higher than those of TiO<sub>2</sub> and ZrO<sub>2</sub> including glass-ceramics. The MTT results showed that glass-ceramic samples were biocompatible. Small addition of additives had a stimulating effect on the cell proliferation.

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