

EFFECT OF Na₂O ON THE CRYSTALLIZATION CHARACTERISTICS AND MICROSTRUCTURE OF GLASS-CERAMICS BASED ON THE CaO–MgO–P₂O₅–CaF₂–SiO₂ SYSTEM

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Submitted January 20, 2009; accepted June 3, 2009

Keywords: Glass; Crystallization; Glass-ceramic; Microhardness

The crystallization characteristics of glasses based on the CaO–MgO–P₂O₅–CaF₂–SiO₂ system containing Na₂O were investigated by means of DTA, XRD, and SEM. The effect of adding 1.5, 3.0, 4.5 and 6.0 mol.% of Na₂O at the expense of MgO on the crystallization characteristics of the glasses, the type of crystalline phases formed and the resulting microstructure were investigated. The main crystalline phases formed after controlled heat-treatment of the base glass were diopside, wollastonite solid solution and fluoroapatite. The addition of Na₂O at the expense of MgO led to the formation of sodium calcium silicate phase which increased with addition of Na₂O. The Vicker's microhardness values (5837–3362 MPa) of the resulting glass-ceramics were decreased by increasing Na₂O-content in the glasses. The obtained data were correlated to the nature and concentration of the crystalline phases formed and the resulting microstructure.

INTRODUCTION

Glass-ceramic materials are polycrystalline solids with a residual glassy matrix leading to a characteristic microstructure that allows achievement of a better performance to abrasiveness and an increased resistance compared to traditional glasses. The microstructure of such material can be also obtained by a sintering process where crystallization and densification of glass particles occur during firing [1].

Calver et al., [2] studied the influence of fluorine content on the crystallization behaviour of CaO–MgO–SiO₂–P₂O₅–F⁻ glassy system. They found that all glasses of composition (50.28 - x) CaO - 7.11MgO - 35.46 SiO₂ - 7.15 P₂O₅ - x CaF₂, where x = 0, 0.4, 4.77 were crystallized to glass ceramic containing apatite and wollastonite phases. Apatite crystallizes at lower temperature than wollastonite, the former favouring bulk nucleation and the latter exhibits surface nucleation.

Mechanism of crystallization of apatite and wollastonite phases were studied by Galliano and Poroto [3] in a glass of composition 44.7 CaO - 4.6 MgO - 34 SiO₂ - 16.2 P₂O₅ and 0.5 CaF₂ wt.%. The glass was heat-treated at 749–851°C to form apatite phase and then at 925–1025°C where the wollastonite phase was crystallized. They also noticed that the initial crystallization of wollastonite was very fast and also increases with temperature.

Salama et al., [4] prepared glass-ceramics from 33.32 CaO - 20.1 MgO - 40.76 SiO₂ - 4.36 P₂O₅ - 1.46 CaF₂ (mol.%), with minor amounts of Na₂O, B₂O₃ and TiO₂. They showed that diopside and fluoroapatite

crystalline phases were the main phases developed. The product has linear expansion coefficient (25–500°C) 10.0 × 10⁻⁶ °C⁻¹ and microhardness value 7085 MPa. Tulyaganov [5] stated that there is no evidence for the formation of solid solution phases or liquid immiscibility gaps between diopside and fluoroapatite phases.

Kokubo et al., [6] succeeded to prepare a high strength glass-ceramics in the CaO–MgO–SiO₂–P₂O₅ system (A-W glass ceramics). They found that the crystallization of the parent glass in a bulk form led to the occurrence of large cracks. This was attributed to the precipitation of fibrous β-wollastonite after precipitation of fluoroapatite, however, crystallization of the same glass in a powder form yielded cracks-free glass-ceramic formed due to the crystallization of both apatite and wollastonite fine crystals throughout the glass article. Shyu & Wu [7] and Liu & Chou [8] have studied the crystallization of glass-ceramic, based on the MgO–CaO–SiO₂–P₂O₅ system. They found that this glass-ceramic system had a superior strength and fracture toughness when compared to the apatite-wollastonite material.

Mastelaro et al., [9] studied the crystallization characteristics of the Na₂O–CaO–SiO₂ system. They detected (Na₂Ca₂Si₃O₉) crystalline phase after heat-treatment at crystallization temperature of 690°C.

The aim of the present work is to study the crystallization characteristics and microhardness of the CaO–MgO–P₂O₅–CaF₂–SiO₂ glass modified by adding Na₂O at the expense of MgO. The relationship between crystalline phases formed, microstructure and microhardness of these glass-ceramics are concerned.

EXPERIMENTAL

Batch Composition and Glass Preparation

In the present work, a systematic study of the crystallization characteristics and microhardness of some glasses based on the CaO–MgO–P₂O₅–CaF₂–SiO₂ system modified by adding 1.5, 3.0, 4.5 and 6.0 mol.% of Na₂O at the expense of MgO are considered (Table 1). The glass batches were prepared from reagent grade powders of CaCO₃, MgCO₃, Na₂CO₃, NH₄H₂PO₄, Quartz (SiO₂) and CaF₂. The components of the batch after being accurately weighed were thoroughly mixed in agate mortar for about 15 min. to ensure complete homogeneity. The weighed batches were melted in Pt–2% Rh crucibles, covered with platinum cap to minimize the evaporation, in an electric furnace with SiC heating elements at 1200–1350°C for 3 h. The homogeneity of the melts was achieved by stirring the melt several times at about 30 min intervals, the melt was cast into rods, squares and buttons which were then properly annealed in a muffle furnace at 650°C for 30 min to relax the stresses.

Table 1. The chemical compositions of the glasses (mol.%).

Glass No.	Oxide Ratios *R	Oxide Contents (mol.%)					
		CaO	MgO	Na ₂ O	P ₂ O ₅	CaF ₂	SiO ₂
G ₁	0.00	31.50	21.50	–	3.50	1.00	42.50
G ₂	0.075	31.50	20.00	1.50	3.50	1.00	42.50
G ₃	0.16	31.50	18.50	3.00	3.50	1.00	42.50
G ₄	0.26	31.50	17.00	4.50	3.50	1.00	42.50
G ₅	0.39	31.50	15.50	6.00	3.50	1.00	42.50

*R = Na₂O/MgO replacement ratio

Differential Thermal Analysis (DTA)

The thermal behaviour of the finely powdered (45–75 μm) glass samples was examined using a SETARAM Labsys™ TG-DSC16. The powdered glass was heated in Pt-holder with another one containing Al₂O₃ as a reference material. A uniform heating rate of 10°C/min was adopted. Data were recorded using a computer-driven data acquisition system. The results obtained were used as a guide for determining the required heat-treatment temperatures applied to induce crystallization of the glasses. The progress of crystallization in the glasses was followed by double stage heat-treatment regimes. The glasses were first heated according to the DTA results at the endothermic peak temperature for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h.

Material Investigation

Identification of the crystal phases precipitating due to the course of crystallization was conducted by X-ray diffraction analysis (XRD) of the powdered

samples. The X-ray diffraction patterns were obtained by using Bruker- AXS D8 Advance, with Ni filtered Cu-Kα radiation. The reference data for the interpretation of the X-ray diffraction patterns were obtained from ASTM X-ray diffraction card files. The crystallization characteristics and internal microstructures of fractured surfaces of the crystalline samples, coated with gold, were examined by scanning electron microscopy (SEM). Representative electron micrographs were obtained by using Jeol, JXA-840 Electron Probe Microanalyzer.

Microhardness Measurements

The microhardness of the investigated samples was measured by using Vicker's microhardness indenter (SHIMADZU, HVM-2 Series, Japan). The eyepiece on the microscope of the apparatus allowed measurements with an estimated accuracy of ±0.5 μm for the indentation diagonals. The specimens were cut using a low speed diamond saw, dry ground using 1200 grit SiC paper and polished carefully using 6, 3 and 1 μm diamond paste to obtain smooth and flat parallel surfaces before indentation testing. At least six indentation readings were made and measured for each sample. Testing was made using a load of 100 g; loading time was fixed for all crystalline samples (15 s). The measurements were carried out under normal atmospheric conditions. The Vicker's microhardness value was calculated from the following equation:

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

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/mm² to MPa by multiplying with a constant value 9.8.

RESULTS

Differential Thermal Analysis (DTA)

The DTA data (Figure 1) of the glasses G₁–G₅ showed endothermic effects at the 700–744°C temperature range. This effect represents the glass transition temperature (*T_g*), at which the atoms begin to arrange themselves in preliminary structure elements preceding crystallization. Exothermic effects at the 915–952°C temperature range indicate that the crystallization reaction takes place in the glass. The DTA data (Figure 1) revealed that the addition of Na₂O at the expense of MgO led to shift of both the endothermic dips and the onset of the crystallization exotherms to lower temperatures.

SEM micrographs of the fractured surfaces, Figures 2–4, showed the effect of replacing Na₂O at the expense of MgO on the microstructure of the glass-ceramic samples (G₁, G₃ and G₅). The SEM micrograph

(Figure 2) of the fractured surface of the crystallized base glass G₁ (free of Na₂O) showed volume crystallization of oriented fine fibrous microstructure by heating at 745°C/5h - 950°C/10h. Figure (3) of sample G₃ (with low Na₂O/MgO replacement ratio) showed volume crystallization of fine fibrous and rounded particles-like growths, which were developed by the crystallization at 720°C/5h - 925°C/10h. Elongated botryoidal with coarse aggregates-like growths were formed in the crystalline sample G₅ (with high Na₂O/MgO replacement ratio) heated at 700°C/5h - 915°C/10h (Figure 4).

XRD Analysis

The X-ray diffraction analysis (Figure 5, Pattern I) revealed that the base glass G₁ heated at 745°C/5h-950°C/10h, crystallized into pyroxene phase of diopside-type CaMgSi₂O₆ (major lines 3.66, 3.22, 2.98, 2.94, 2.88, 2.56, 2.50, Card No.19-239), together with wollastonite-like phase (wollastonite ss) (major lines 3.32, 3.22, 2.98, 2.88, 2.56, 2.50, 2.45, 2.34, 2.31, 2.14, 1.82, Card No.29-372) and fluoroapatite phase (lines 3.45, 2.81, 2.77, 2.71, 2.13, 1.82, 1.75, 1.72, Card No.15-876).

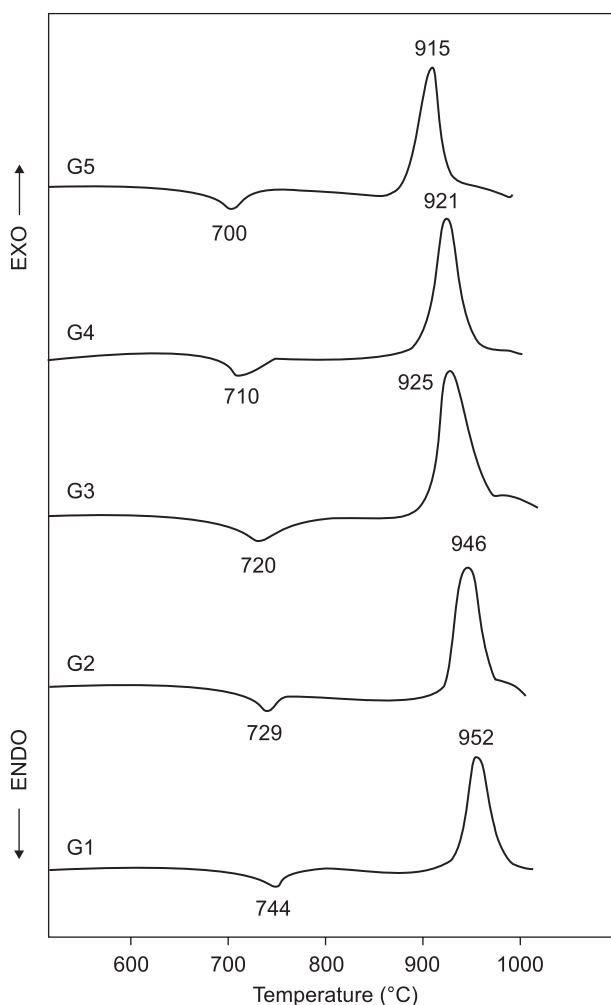


Figure 1. DTA data of the studied glasses.

At low Na₂O/MgO replacement ratios (0.075 and 0.16), i.e. G₂ and G₃ heat-treated at 730°C/5h - 945°C/10h and 720°C/5h - 925°C/10h, respectively, the X-ray diffraction analysis of the crystallization products revealed that diopside-CaMgSi₂O₆, wollastonite ss and

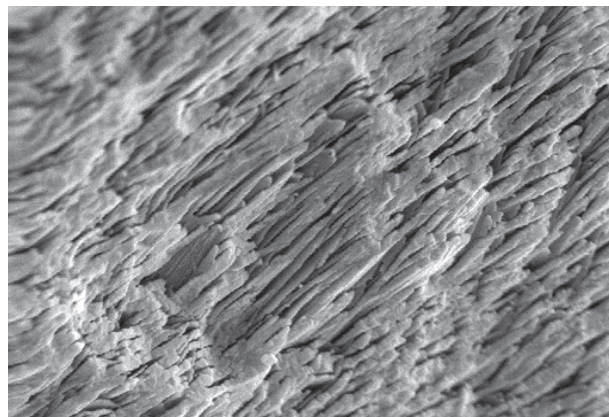


Figure 2. SEM micrograph of fractured surface of base glass (G₁) crystallized at 745°C/5 h and 950°C/10 h, showed volume crystallization of oriented fine fibrous microstructure. Magnification 2000.

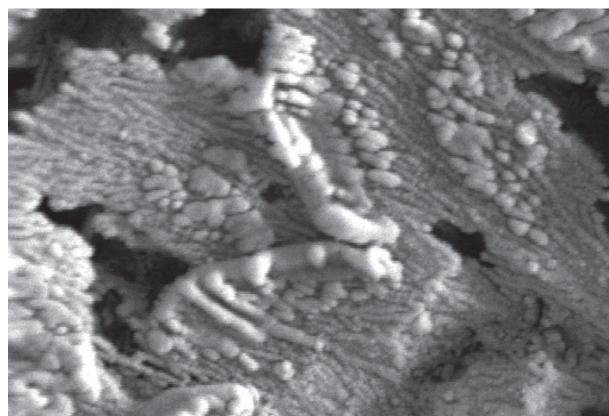


Figure 3. SEM micrograph of fractured surface of glass (G₃), crystallized at 720°C/5h and 925°C/10h, showed fine fibrous and rounded particles-like growths. Magnification 2000.

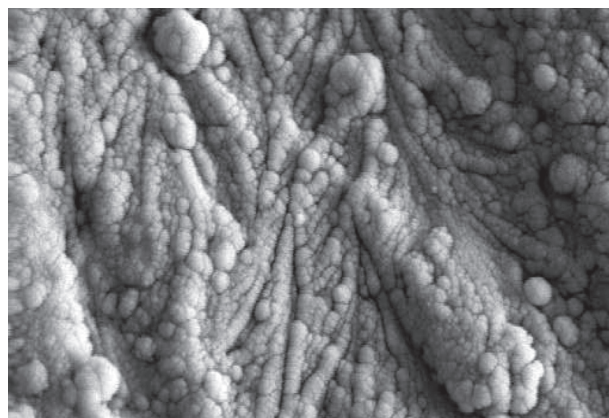


Figure 4. SEM micrograph of fractured surface of glass (G₅), crystallized at 700°C/5h and 915°C/10 h, showed volume crystallization of elongated botryoidal with coarse aggregates-like growths. Magnification 2000.

fluoroapatite- $\text{Ca}_5(\text{PO}_4)_3\text{F}$ phases were crystallized and no Na-containing phases could be detected (Figure 5, Patterns II and III, Table 2).

On increasing the $\text{Na}_2\text{O}/\text{MgO}$ replacement ratio up to (0.26), i.e. G_4 , heat-treated at $710^\circ\text{C}/5\text{h} - 920^\circ\text{C}/10\text{h}$, the X-ray diffraction analysis (Figure 5, Pattern IV) revealed that diopside, wollastonite ss, fluoroapatite and

minor amount of sodium calcium silicate - $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$, (major lines 3.30, 3.05, 2.67, 2.19, 2.18, 2.15, 1.80, 1.65, 1.60, Card No.22-1455) phases were developed.

At high $\text{Na}_2\text{O}/\text{MgO}$ replacement ratio (0.39), i.e. G_5 , heat-treated at $700^\circ\text{C}/5\text{h} - 915^\circ\text{C}/10\text{h}$, sodium calcium silicate phase was increased as indicated by the X-ray diffraction analysis (Figure 5, Pattern V).

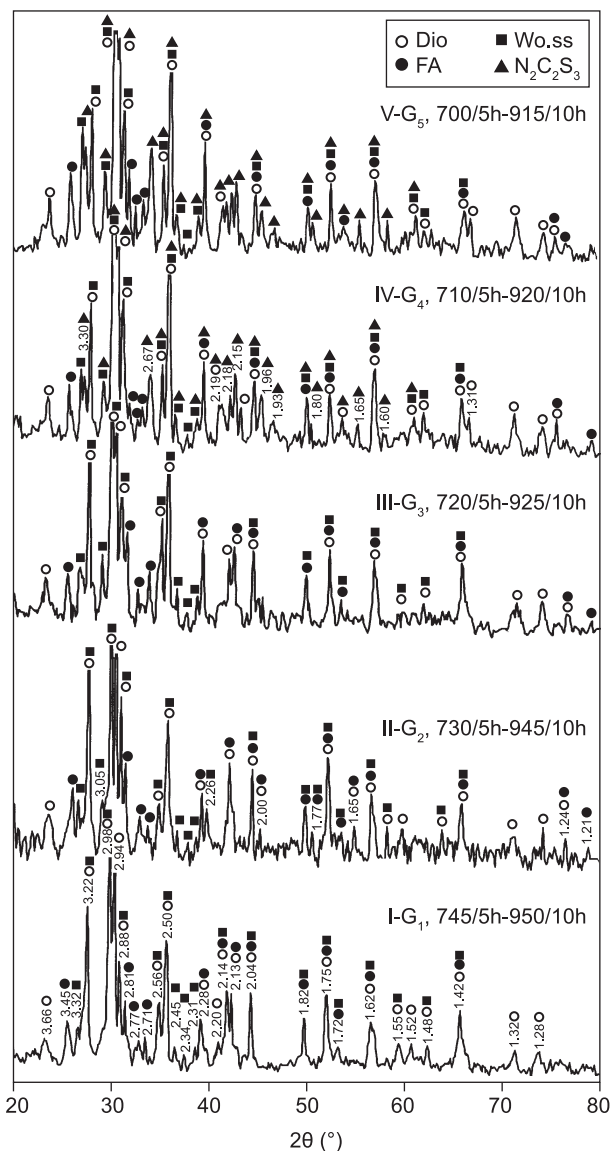


Figure 5. XRD patterns of the studied glass-ceramics (i.e. G_1 - G_5).

Microhardness

The microhardness values of the investigated glass-ceramic materials were exhibited in Table 2. The data are also graphically represented in Figure 6 from which the following outlines could be concluded:

The addition of Na_2O at the expense of MgO in the base glass (G_1) generally led to decrease the microhardness values of the crystalline samples (e.g. G_3 and G_5). The value of sample G_5 (with high Na_2O content) exhibits the lowest hardness value, while the value of the sample G_1 -free of Na_2O represents the highest value (Table 2, Figure 6).

DISCUSSION

Crystallization Characteristics

The Crystallization Characteristics of the Base Glass

The crystallization process of the glass during the reheating process is known to be connected with the nature and proportions of the glass oxide constituents.

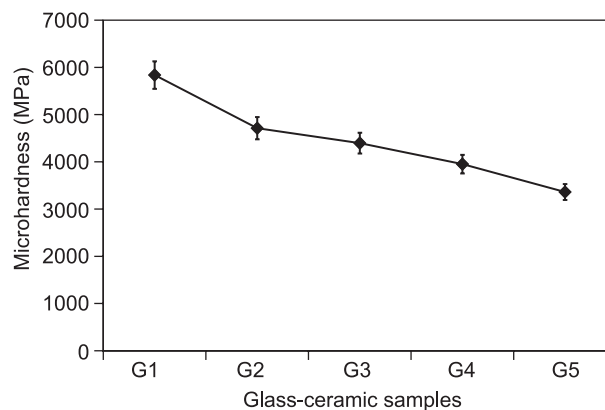


Figure 6. Microhardness values of the studied glass-ceramics (i.e. G_1 - G_5).

Table 2. The crystalline phases developed and microhardness values of the investigated glass-ceramics (i.e. G_1 - G_5).

Glass No.	Heat-treatment ($^\circ\text{C}/\text{h}$)	Microhardness (MPa)	Developed Phases
G_1	745/5h-950/10h	5837 ± 5	Diopside + Wollastonite ss + Fluoroapatite
G_2	730/5h-945/10h	4713 ± 5	Diopside + Wollastonite ss + Fluoroapatite
G_3	720/5h-925/10h	4396 ± 5	Diopside + Wollastonite ss + Fluoroapatite
G_4	710/5h-920/10h	3951 ± 5	Diopside + Wollastonite ss + Fluoroapatite + Sodium calcium silicate (minor)
G_5	700/5h-915/10h	3362 ± 5	Diopside + Wollastonite ss + Fluoroapatite + Sodium calcium silicate (increased)

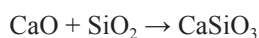
The ability of some cations to build glass forming units or to be housed as modifiers in interstitial positions in the glass structure must also be considered [10].

The sequence of the phases development during crystallization of the base glass, (G₁) revealed that diopside-CaMgSi₂O₆ was formed as a major phase together with wollastonite solid solution and fluoroapatite-Ca₅(PO₄)₃F phase.

Theoretically, on the basis of the petrochemical calculation of normative mineral molecules [11] it was found that diopside-CaMgSi₂O₆, can be formed as a major constituent, while wollastonite-CaSiO₃ and fluoroapatite-Ca₅(PO₄)₃F phases are crystallized as secondary phases from crystallization of the base glass G₁. However, the present results revealed that wollastonite solid solution phase was developed instead of wollastonite phase as indicated from the shift of d-spacing lines (XRD) characteristics for wollastonite phase towards higher 2θ values. Thus, during crystallization of the glass, CaO can combine with equivalent amount of MgO together with the proper amount of SiO₂ to form diopside according to the following schematic equation:



The remaining CaO present in the glass can combine with the corresponding amount of the remaining silica to form wollastonite as follows:



It seems, therefore, that wollastonite can accommodate diopside molecule in its structure to form wollastonite solid solution (ss). Deer et al. [12] reported that wollastonite can take up to 22 percent of diopside (CaMgSi₂O₆) phase in its structure. It assumed therefore that the preferential formation of wollastonite solid solution phase was favoured by the great affinity of the wollastonite to accommodate the diopside component in solid solution.

Toya et al. [13] have reported that diopside is a preferable crystalline phase since it results in stronger materials than glass-ceramics based on wollastonite.

The Effect of Substitution of MgO by Na₂O

The Na₂O/MgO replacements in the base glass progressively enhanced its crystallization tendency, the endo- and exotherms of the glasses are affected and displaced toward lower temperatures. This may be explained by the lowering effect of Na₂O on the viscosity of these glasses [5].

Denry and Holloway [14] reported that sodium acts as a glass network modifier capable of lowering the viscosity of silicate glasses by increasing the number of non-bridging oxygen in glass composition. As a result of the decrease in the viscosity, the mobility and diffusion rates of the different ions and ionic complexes forming glasses during the crystallization process will be markedly increased, leading to higher crystallization

tendency. Baldi et al., [15] and Tulyaganov et al., [16] reported that the addition of Na₂O plays an important role in lowering the melting point of the glasses and enhancing sinterability.

At low additions of Na₂O instead of MgO, diopside, wollastonite ss and fluoroapatite phases were crystallized and no Na-containing phases could be detected. From the mineralogical point of view, the presence of Na₂O in a small amount generally did not lead to the formation of sodium-containing phases. It was suggested, therefore, that Na₂O could be present in the glassy matrix of the resultant glass-ceramic [17].

On increasing the Na₂O/MgO replacements, i.e. G₄ and G₅ crystallized to diopside, wollastonite ss and fluoroapatite phases in addition to sodium calcium silicate- Na₂Ca₂Si₃O₉ phase which increased with Na₂O additions.

Microhardness

Hardness is not a fundamental physical property of material but it rather depends on several properties. Its interpretation varies considerably depending on the nature of the material under examination and the method of test under consideration. Therefore, the resistance of the material to abrasion under closely specified conditions may be taken as one measure of hardness [18].

Henry and Hill, [19] reported that the microstructure mostly represents the major influence on the mechanical properties of the glass ceramic materials. They found that hardness of fluorosilicate glass-ceramics decreased markedly due to the development of the coarse microstructure in the glass-ceramics. The mechanical properties of glass-ceramics, among others variables, depend on volume fraction, grain size, crystal phase and shape of crystals [20].

In the present work, high microhardness value (5837 MPa) was determined for the crystalline base glass, G₁, due to the formation of oriented fine fibrous microstructure as indicated from SEM (Figure 2) and also to the crystallization of high microhardness diopside phase (major), together with wollastonite ss and fluoroapatite phases. Park et al., [21] indicated that glass-ceramics containing large amount of diopside phase generally showed a high microhardness value due to the interlocking microstructures of diopside crystals with microhardness value 6730 MPa. Sohn et al., [22] revealed that the hardness of silicate glass-ceramics increased due to the fine grained microstructure by which the crystal size plays an important role in preventing the propagation of the cracks in the whole structure. The microhardness of glass-ceramics generally increased with the crystallization amount, smaller crystalline grains as well as formation of fine microstructure [23].

The addition of Na₂O at the expense of MgO in the base glass (G₁) decreased the microhardness values of

the investigated glass-ceramics (G_2 - G_5). This may be due the formation of coarse grained microstructure, of rounded and botryoidal-like growths as indicated from the SEM micrograph of (e.g. G_3 and G_5 & Figures 3 and 4). This is as compared with that of fine microstructure formed in the crystalline base glass G_1 (Figures 2).

The obtained data revealed that the investigated glass-ceramics had microhardness values (5837-3362 MPa) while the microhardness value of natural teeth enamel (3600 MPa) [24]. This means that the studied glass-ceramics can be used as alternative core materials in dental applications [25].

CONCLUSIONS

The crystallization characteristics and microhardness of the glass-ceramics based on the $\text{CaO-MgO-P}_2\text{O}_5\text{-CaF}_2\text{-SiO}_2$ system, modified by adding Na_2O at the expense of MgO were investigated. The addition of Na_2O at the expense of MgO in the base glass had an effect on the crystallization products and microstructures of the resulting glass-ceramic. Diopside (major), wollastonite ss and fluorapatite phases could be obtained together with sodium calcium silicate phase which increased with further Na_2O additions. The types of the crystallized phases formed and their microstructures were discussed in relation to the compositional variation of the parent glasses. The microhardness values (5837-3362 MPa) of the investigated glass-ceramics were markedly decreased with the addition of Na_2O at the expense of MgO and the studied glass-ceramics can be used as alternative core materials in dental applications.

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