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Characterization of bioglass ceramic after addition of fluorine in Na_2O-CaO-SiO_2 system

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ABSTRACT

Bioactive glass formed on the base sample (G_o) of 45S5 system with fluorine additives samples were prepared by melt quenching method. The glassy samples were subjected to DTA for determining temperatures at which phase transition occur. FTTR spectroscopy shed a light on the sorts of compounds, their structure as well as their functional groups. The crystalline nature of samples was confirmed by XRD. The calculation of crystal size X_c revealed that the addition of fluorine as a network modifier didn't affects the phase formation when the phase $Na_2CaSi_3O_8$ was formed which is similar to the phase developed within the base sample (G_o) the addition of fluorine also caused a shift of the glass transition temperature (T_g) °C, softening temperature (T_s) °C, and crystallization temperature (T_c) °C to lower values.

Key words: Bioglass ceramic, Fluorine, crystalline, DTA.

INTRODUCTION

The composition of the first bioactive glass was created and tested by Hench, 1998. Hench discovered that the glasses containing 45% (SiO_2 45; Na_2O 24.5; CaO 24.5; P_2O_5 6 wt %) form a mechanically strong bond with bone. [1], it has been proven that other ceramics also show enhanced ability to bond with soft tissues. Examples include certain compositions in this family of bioactive glass, which affects the rate of formation of glass and glass ceramics [2,3,4,5] as well as sintered hydroxyapatite. All of these types of glass are called bioactive ceramics. Implants made layer react chemically with body fluids in a manner compatible with the repair processes of the tissues. The disadvantage of this glass is its brittleness which limits their use for load bearing implants. This can be overcome by converting this glass into glass ceramic, by using it as coating on metallic surfaces or by adding different modifiers[6,7].

Cheng et al. Studied the Effect of fluorine content on the crystallization of glass, they noticed that the glass transition temperature (Tg) shifts to low temperature as the fluorine content increases. This because the Tg is related to the viscosity of the glass and determined by the structure of glass. The incorporation of F−in the glass network results in the substitution of one Si-O-Si bond by two Si-F bonds. The glass network is broken at Si-F bonds Therefore, the higher the F− content is, the more Si-F bonds are generated, the lower the viscosity and T_g[25].

The effect of calcium fluoride (CaF_2) on the chemical solubility of an apatite–mullite glass–ceramic material was studied by Hawa Fathi H. et al. and found that the increasing of CaF_2 content increases chemical solubility for the as-cast glass, apatite and apatite–mullite phases[12].

The aim of the present work is to examine the bioactivity of prepared and their corresponding glass ceramic and modifying their structure by addition of fluorine.

MATERIALS AND METHODS

(a) Preparation of glass powder

Two different samples of glasses were prepared, and as a reference G_o , a glass with the composition corresponding to bioglass 45S5 was also prepared as shown in table 1.

About 100 g of each batch were prepared by mixing reagent Ca-(H_2PO4) H_2O, $CaCO_3$, $NaHCO_3$, SiO_2, CaF_2 and NaF, homogenous mixtures of batches obtained by dry mixing for 0.5 hours in a high-speed porcelain ball miller. Mixed batches were preheated in a platinum crucible for 1 h at 1050^0C to derive off the volatile components and for de-carbonization, after each drying step the powder was reground to ensure homomgeneity; and then melted in platinum crucible at 1300^0C for 2 hours. Glass in frit form was obtained by quenching melt in cold water to prevent phase separation. The frits were dried and then dry milled at high speed porcelain ball miller for 0.5 h to obtain the glass in a powder of particle size (53-106) µm which is suitable for DTA measurements.

Table (1) The different additives on the Na_2O-CaO-SiO_2-P_2O_5 glass system

Glass sample	45S5 glass				Additives	
	Na_2O	**CaO**	**SiO_2**	**P_2O_5**	**NaF**	**caF_2**
G_o	24.5	24.5	45	6	-----	-----
G5C	24.5	24.5	45	6	-----	5
G5N	24.5	24.5	45	6	5	-----

g/100 g glass oxide

(b) Differential Thermal Analysis (DTA)

The thermal behavior of the glassy powder was carried out using the DTA analysis to determine temperatures degrees at which phase transitions occur. The samples with the weight of 50 mg were analyzed by DTA measuring system Labsys TG™-DSC16 furnace with heating rate of 10 ^{o}C/min the data were recorded by means of a chart recorder.

(c) X-ray diffraction (XRD) measurements

After two steps heat treatment, glassy samples were examined with a light-resolution X-ray powder diffractometer using monochromatic CoKα radiation (λ=1.79026 A^o). X-ray diffraction patterns have been recorded with scanning rate of 0.1^o in the 2θ ^{o} ranging from 10 to 80^o per s step. The results have been used to insure the glass state formation and flowed by heat treatment of glass samples, to determine the crystal structure of the glass-ceramic samples. Silicon was used as standard material to calibrate the instrument.

(d) Evaluation of crystallinity

The degree of crystallinity, corresponding to the fraction of crystalline phase present in the sample, was evaluated by the relation:

$$X_c = 1- (V/I) \qquad (1)$$

Where
V: the intensity of the hollow between the main peak and peak besides it.
I: the intensity of the main peak.

(e) Determination of crystallite diameter(nm)

To determine the crystallite diameter Scherrer equation was applied

$$L = K \lambda /\beta \ \mathrm{Cos}\theta \qquad (2)$$

Where
L: the average crystallite size,
β: the full width of the peak at half of maximum intensity (FWHM)
λ: is the wavelength of monochromatic X-ray beam CoKα radiation (λ=1.79026 A^o),
θ: the peak diffraction angle, and K: the Scherrer constant defined as the crystallite shape and is approximately = 0.9.

(f) Determination of Density

The value of experimental density for glass was measured by Archimedean's technique at room temperature with de-ionized water as the immersion medium, which has density=1 g/cm^3, by using the following equation:

$$\rho_{ex} = \left(\frac{W}{W - W_w} \right) . d_w \qquad (3)$$

Where
ρ_{ex} : is the experimental density of the glass sample.
W: is the weight of glass sample in air.
W_w: is the the weight of glass sample in de-ionized water.
d_w: is the density of the distilled water.

(e) Determination of the molar volume
The molar volume of samples was determined by using the following formula:

$$V_m = \frac{M}{\rho} \qquad (cm^3 / mol) \qquad (4)$$

V_m: is the molar volume,
M: is the molecular weight in (g/mol) and
ρ: is the density in (g/cm^3).

RESULTS AND DISCUSSION

DTA results

The DTA results are presented in Fig. (1) and summarized in table.2. From it was observed, that, the incorporation of fluorine in the base glass decreased the glass transition temperature T_g^o C, softening temperature Ts^o C, and the crystallization temperature (Tc), according to the values shown in table (2).

Table (2), DTA analysis for prepared glassy samples

Glass sample	DTA results			Fluorine Additives
	T_g°C	T_s°C	T_c°C	
G_o	520	540	692	1350
G5C	495	512	655	1320
G5N	440	485	630	1300

Fig.(2) shows the DTA curves of fluorine containing samples compared to the base sample (G_o).The decrease of the transition temperature upon addition of fluorine may be attributed to the backbone of the glass silicate structure in the SiO_4 tetrahedral network. These SiO_4 tetrahedral are connected at the corners to form a continuous 3D network. The inclusion of fluorine in the glass network leads to substitution of Si - O -Si bond by two Si-F bonds (two non-bridging fluorine). The glass network is broken at Si-f bonds.

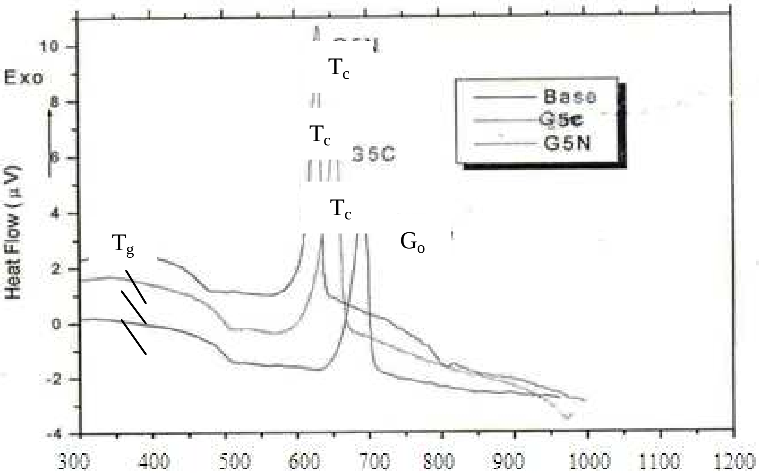


Fig.(1) DTA curves of fluorine containing samples compared with that of the G_o

Therefore the incorporation of Fluorine - in the form of CaF_2 and NaF leads to modifying and weakening the network, lowering the viscosity of the melt, transition temperature T_g softing temperature T_s and crystallization temperature T_c ^{o}C.

Analysis of X-ray diffraction (XRD)

Following the observed DTA results, glass samples were subjected to heat treatment by following two steps at different temperatures depended on their softening and crystallization temperatures that were observed by DTA. One of these temperatures for nucleation and the other for crystal growth in order to obtain the corresponding glass ceramic[8]. X-ray diffraction is a helpful tool for determining and identifying the crystalline phase in the glass-ceramics.

The XRD patterns of fluorine containing glass ceramic samples G5C and G5N after being heated at 500/3h and 700/3h ^{o}C are shown in Fig. 2. The observed phase degree of crystallinity and crystal diameter are summarized in table (3).

From fig (2), it is observed that the major phase was identified as $Na_2CaSi_3O_8$ in both fluorine containing samples G5C and G5N. These results showed that angular location match the standard PDF (card number: JCPDS# 12-671), the same crystalline phase has been formed and identified in previous studies of heated bioactive glass [9]. These results mean that the incorporation of fluorine have no effect on the phase formation since the same phase $Na_2CaSi_3O_8$, was detected within the base sample G_0. There is only a slight shift of the main peaks to high angle. This may attributed to the ionic radius of sodium (0.97A^{0}) which is nearly the same as the calcium ionic radius (0.99 A^{0}) ,So by adding the fluorine as network modifier the fluorine F- will replace the oxygen O- in the network [10]. It was also observed that addition of fluorine into the base sample cause broadening of the peaks, this attributed to the decrease in the grain size, it is believed that fluorine has high nucleation rate and consequently has a relatively small crystal growth [11].

From table (3), it was observed that the degree of crystallinity is higher for fluorine containing samples. In this trend the crystallinity for G_0, G5C and G5N is 96.17, 97.6 and 96.63 % respectively. This means that fluorine addition lead to decrease of the viscosity so it acts as a facilitator of the kinetics of crystallization by allowing motion and rearrangement of the glass network [13].

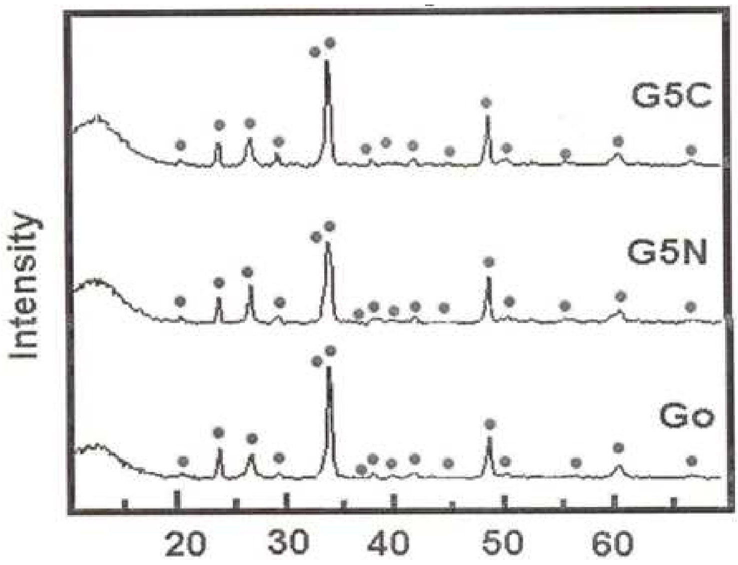
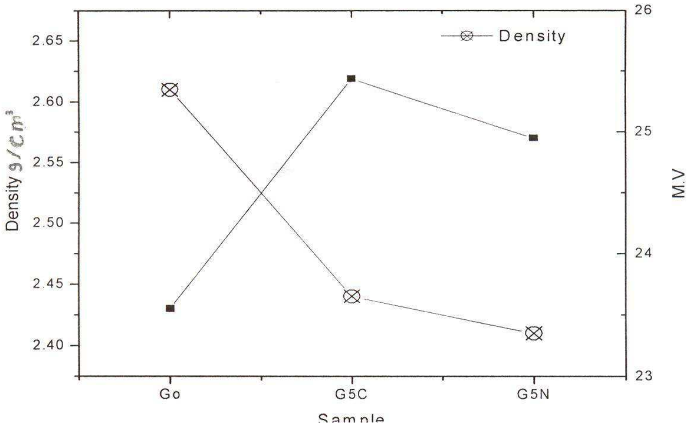


Fig (2), X-ray diffraction patterns of G_0, G5N and G5C powder sintered at 500 ^{o}C/3h and 700 ^{o}C/3h [:$Na_2CaSi_3O_8$ phase]

Table (3), Identified phases, crystal diameter and degree of crystallinity after heated the glass samples containing fluorine at same thermal conditions

Sample	Phase developed	Degree of crystallinity %	Crystal diameter (nm)
G_0	$Na_2CaSi_3O_8$	96.17	211.8
G5C	$Na_2CaSi_3O_8$	96.72	184.2
G5N	$Na_2CaSi_3O_8$	97.26	131.8

Density is an important property of matter and it is essential for understanding and controlling glass and glass ceramic manufacture .Figures (3), shows the relation of experimental density and molar volume for fluorine containing glass samples . From table (4) it is quite clear that the fluorine containing sample G5C & G5N exhibit lower density and higher molar volume than that of the base sample G_0. The decrease of density can be explained by the increase of network disruption with the increasing of fluorine content. This in turn leads to a less dense structure, and an enhancement of volume which causes a lower density of fluorine containing glass samples and its glass ceramics G5C & G5N [14].



Sample

Fig. (3) Values of experimental density & molar volume of G5c & G5N, fluorine containing glass samples compared with the base sample

CONCLUSION

Addition of fluorine to glass and glass-ceramic samples leads to:

- Modifying and weakening of the network, lowering the viscosity of melt, transition temperature Tg, softening temperature Ts, and crystallization temperature Tc ^{0}C.
- Formation of the phase $Na_2CaSi_3O_8$ which was detected within the base sample. i.e. no effect on phase formation.
- Higher degree of crystallinity for samples of greater fluorine content.
- Lower density and higher molar volume than that of the base sample.

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