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Effect of sintering time on crystallization, densification and in-vitro characteristics of bioactive glass ceramics

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Abstract: ***In order to improve the chemical stability and modify the biodegradability of bio-glass ceramics materials for certain applications, a correlation between structural and biological properties of bio-glass ceramics is very essential and these properties are found to be greatly dependent on the composition and synthetic parameters of the material. In the present work, an attempt has been made to study the effect of sintering time on crystallization, densification and in-vitro properties of a new glass ceramics system. For that purpose, glass of the composition (% wt) ($34SiO_2$-46CaO-$14.5P_2O_5$-$4Na_2O$-$1CaF_2$-.$5MgF_2$) was prepared by melting the thoroughly mixed powders of the ingredients in muffle furnace and then quenching the melt in water. Sintering was carried out at 1000 ℃, in accordance with the average of three exothermal peaks of differential thermal analysis (DTA), for three different time intervals 5h, 10h and 15 hours respectively. The main crystalline phases formed after controlled heat-treatment of the glass were hydroxyfluoroapatite (HFA), tricalcium phosphate (TCP) and wollastonite (W) respectively as conformed by the X-Ray diffraction (XRD). Scanning electron microscope, bulk density and diameter shrinkage co-efficient data illustrated that the rate of densification was higher for 5-10 hours sintering time interval than that for 10-15 hours. At 15 hours sintering time, decomposition of HFA into TCP and W was also observed. The samples were immersed in simulated body fluid (SBF) for 30 days at ambient temperature. Fourier transformation infrared spectroscopy (FTIR) and energy dispersive analysis by X-rays (EDX) revealed the presence of Hydroxycarbonate apatite (HCA) showing that the glass ceramics under investigation were bioactive and their bioactivity depends on the sintering time.***

Index Terms: **Hydroxyfluoroapatite, Tricalcium-phosphate, Bioactivity, Densification.**

I. INTRODUCTION

Glass ceramics are the polycrystalline solid materials prepared by the controlled crystallization of parent glasses according to the desired set of biological, structural and mechanical properties. Bioactive glass ceramics own the ability to make a bond with the bone tissues in physiological environment [1]. Bioactivity of glass ceramics is measured by the rapidity of development of hydroxy-carbonate apatite (HCA) and its bonding with the surrounding tissues [2, 3]. Their bonding ability is lesser than that of bio glasses but greater than bio ceramics. The well known bioactive glass ceramics in orthopedics applications are calcium phosphate based hydroxyapatite-containing glass ceramics having chemical resemblance to the inorganic component of bone and teeth. Small variations in Ca/P ratios of calcium phosphate glass ceramics cause to change the structural and biodegradation behaviour of the glass ceramics [4,5]. Apatite-Wollastonite containing glass ceramics (A-W GC) are also well known for having *in vitro* and *in vivo* stability and are difficult to be resolved in physiological fluids [6]. Bioactive glass ceramics containing apatite and wollastonite phases are found to have good mechanical properties like bending strength, fracture toughness and young's modulus etc, enabling to be used in load bearing applications such as vertebral prostheses etc [7-11].

Although, there is a great strategical significance of glass ceramics in the field of bio-materials, yet there is a lack of detailed study on the correlation between the structure and the activity of a glass composition in a biological surroundings that negatively affects further progress, in improving the chemical stability and modifying the biodegradability of these materials for certain applications so there is a need to prepare and characterise new bio-glass ceramics materials using every possible compositional and parametric changes because bioactivity and structural properties of glass ceramics are found to be greatly affected by these important variations [7,12]. Keeping it in mind, in our previous papers we have studied the effect of CaO/MgO ratios on structural and mechanical properties of bio-active glass ceramics and effect of sintering temperature on structural and in-vitro behaviour of bioactive glass ceramics [13,14], besides that we have also studied the

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dissolution behaviour of bioactive glass ceramics with different CaO/MgO ratios [15]. In continuation of that work, now we prepared the glass ceramics of the same composition ($34SiO_2$-46CaO-$14.5P_2O_5$-$4Na_2O$-$1CaF_2$-.$5MgF_2$) [13,14] by melting the thoroughly mixed powders of the ingredients in muffle furnace, quenching the melt in water and sintering the glass compacts at 1000 °C, according to the average of DTA data, for three different time intervals 5h, 10h and 15 hours respectively. Structural characterization is carried out employing thermal analysis using DTA, crystallization studies using XRD and bulk densification and surface morphological studies using SEM. EDX and FTIR are used to investigate the *in vitro* behaviour of the glass ceramic samples after immersion in SBF for 30 days.

II. MATERIALS AND METHODS

A. Synthesis

99.9% pure powders of composition (% wt) $34SiO_2$-46CaO-$14.5P_2O_5$-$4Na_2O$-$1CaF_2$-.$5MgF_2$ were thoroughly mixed in agate mortar and pestle for several hours. The powder was placed in Platinum crucible and was put in muffle furnace for melting at 1500°C. This temperature was achieved at ramp rate of 5°C per minute. In the furnace, this temperature was held stable for two hours to achieve sufficient liquid flow of melt and homogeneity and finally the melt was quenched into water. The whole process took about seven hours. The frit was dried and again pulverized for several hours using mortar and pestle. The new formed powder was melted again by the same method as mentioned above and fine homogenous powder was finally achieved. 5 wt% Polyvinyl Alcohol (PVA) was mixed as organic binder for compaction. The mixture was compacted under a pressure of 10 tons / cm^2 in a hydraulic press to form pellets of 12 mm diameter. The pallets were sintered at 1000 °C, according to the average of Differential Thermal Analyzer (DTA) data, for three different time intervals 5h, 10h and 15 hours, each in a muffle furnace. The samples were named GC_1, GC_2 and GC_3 respectively. The temperature of the furnace was raised at the ramp rate of 5 °C /min beginning from the room temperature. Temperature was maintained at 700 °C for 1 hour for the creation of nucleation sites in each sample before the sintering temperature i.e; 1000°C. The furnace was switched off at the end of each sintering process till the room temperature was achieved and samples were taken out.

B. Characterization

1) Structural characterization

Structural characterizations of the glass ceramic samples were carried out by various techniques. Thermal analysis was carried out on glass powder by Differential Thermal Analyzer (DTA) (SDT Q600 V8.0 build 95) from room temperature to 1400 C° with ramp rate of 5 C°/min to investigate the endothermic and exothermic peaks of different phases and the thermal stability of the glass.

PAnalytical X'Pert PRO MPD θ–θ X-ray diffractometer (XRD) operating at a voltage of 40 kV and a current of 40 mA using a CuKα (λ=1.540598 Å) radiation source was used to study the various crystalline phases of the glass ceramic samples sintered at 1000 C° for different time intervals. Crystallite sizes of the dominant crystalline phases were calculated using the Scherer formula [16]

Crystallite size = $K\lambda/(FWHM\ Cos\theta)$

where λ=1.54 Å is the wavelength of the X-ray, FWHM is the full width at half maxima (in radian) of the particular diffraction peak, θ is the corresponding Bragg's angle of the diffraction peak and k is the Scherrer constant equal to 0.89.

The density ρ of the glass ceramic samples was calculated using Archimedes principle [17], using water as an immersion liquid:

$\rho = \alpha\rho_w/(\alpha\text{-}b)$

Where ρ_w is the density of water, α is the mass of the sample in air and b is the mass of the sample in water.

The diameter shrinkage coefficient [2] was calculated as gradient of the plot of $\Delta D = (D\text{-}D_0) / D_0$ vs sintering time T, where D is diameter of the sintered sample at time T and D_0 is diameter at the start of experiment.

The morphology of the ceramic samples was studied using Scanning Electron Microscope (SEM) (JEOL, JSM 840A) using secondary electron mode of imaging. The grain size was calculated by the intercept method [18].

2) *In Vitro* study

The glass ceramics samples were investigated for bio-compatibity by immersing in simulated body fluid (SBF) for 30 days at ambient temperature. Energy Dispersive analysis by X-rays (EDS) (JEOL, JSM 840A) and Fourier Transformation Infrared Spectrometer (FTIR) (Bruker, model Vector 22) were employed for the *in vitro* characterization.

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III. RESULTS AND DISCUSSION

A. Structural Characterization

DTA graph of the glass powders is shown in Fig 1. There is an endothermic peak at about 270 °C which indicates the elimination of the organic binder used for efficient compaction. These Oxygen bonds are broken by divalent cations Ca^{2+} and Mg^{+} as network modifiers as well as by the internal strains due to the difference of covalence of the bonds joined by oxide bridges [21]. Three exothermic peaks of DTA graph describe that the glass is of multi phase nature. These peaks might be attributed to Hydroxyfluoroapatite (HFA) ($Ca_5(PO_4)_3(OH)F$), Tricalcium Phosphate (TCP) ($Ca_3(PO_4)_6$) and Wollastonite (W) ($CaSiO_3$) crystalline phase as shown by the XRD data.

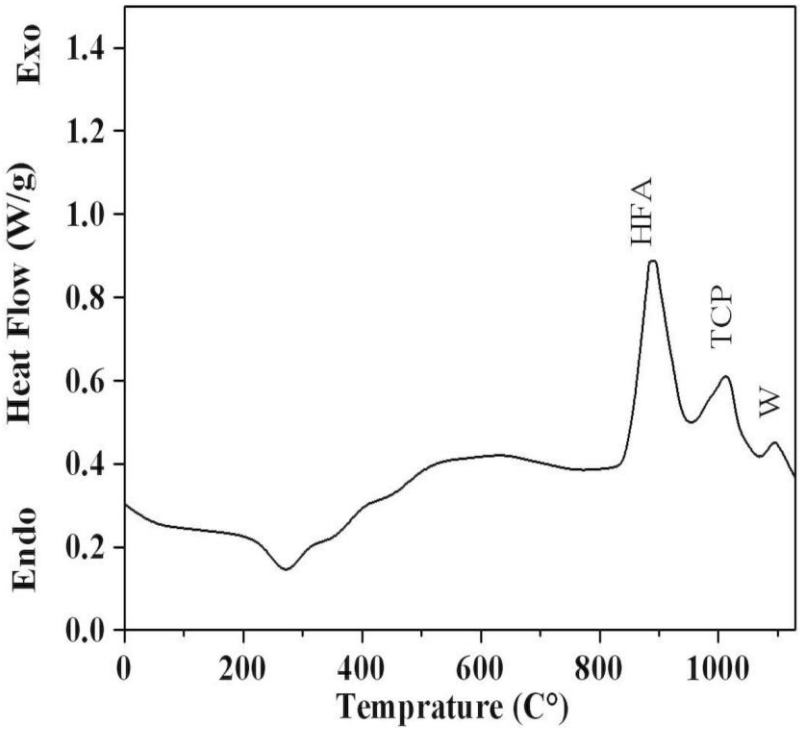

Fig 1. DTA graph of Glass powders

Fig 2 shows the XRD graphs of GC_1, GC_2 and GC_3. Graph of GC_1 indicates that the HFA phase is the most prominent with minor traces of TCP and W at 5 hours sintering time interval. Mg^{2+} ions may have a role to make the glass network loose and unstable to cause the crystallization during this short sintering time interval [22]. Graph of GC_2 shows a regular increase in the peak intensities of HFA and W but the most efficient crystals growth is of TCP which is due to the relatively higher sintering time interval. Graph of GC_3 has the most efficient crystallization of W. During 15 hours sintering time interval, the fraction of TCP phase increases while that of HFA decreases which may be due to the decomposition of HFA into TCP and W at high sintering time interval [2,19,20]. HFA has to give out water for the formation of TCP which may be taken up by SiO_2 and helpful in the formation of W at silica rich sites. The variation of dominant peak intensities of these phases with sintering time interval is shown in fig 3. Gradient of the curve of TCP is much higher than those of HFA and W in the domain 5-10 hours sintering time interval whereas slope of the curve of W is the most prominent in the later time interval. Intensity of the HFA peaks decreases in the later range which is probably due to its slight decomposition into TCP and W at higher sintering time intervals. Variation of crystallite size against sintering time interval (Fig 4) is also in accordance with the intensity plot.

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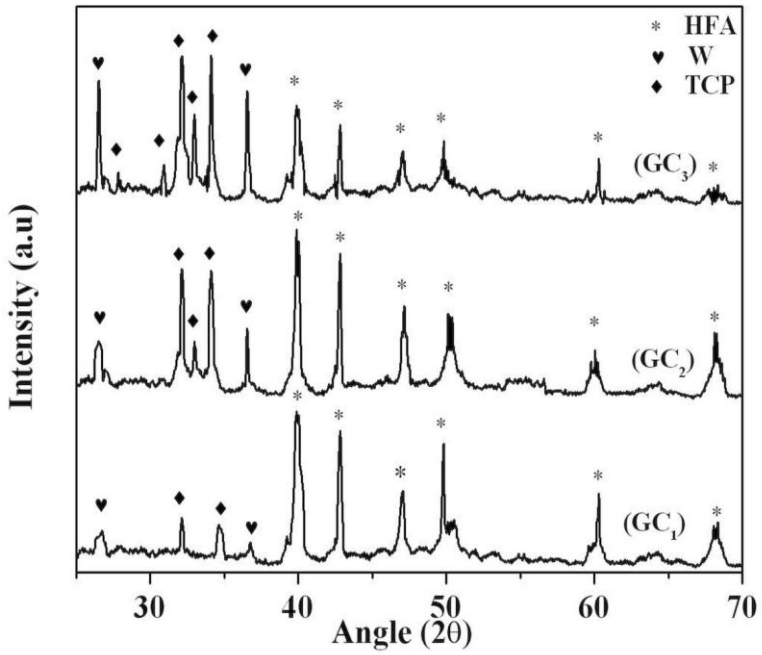

Fig 2. XRD graphs of samples GC_1, GC_2 and GC_3

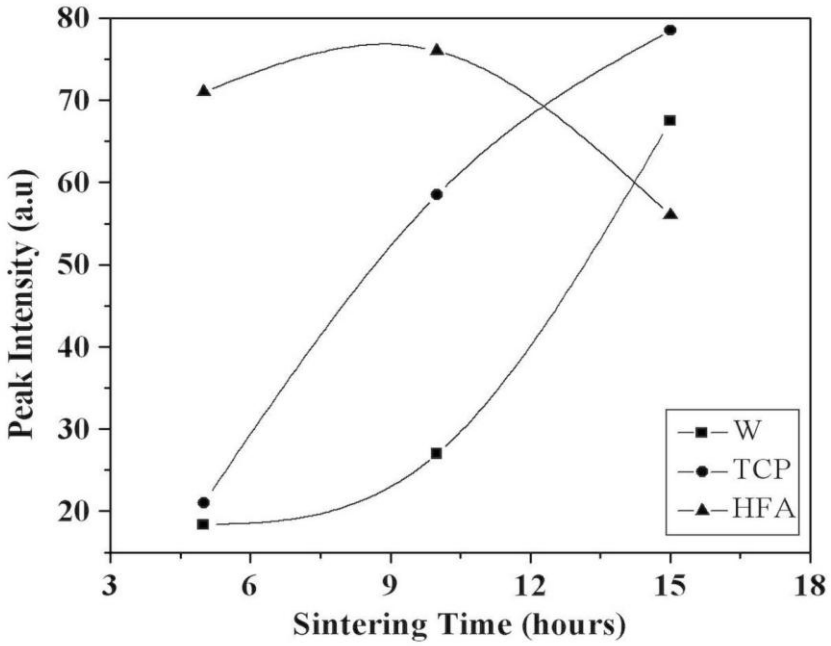

Fig 3. Variation of XRD Peaks Intensity with Sintering Time Interval

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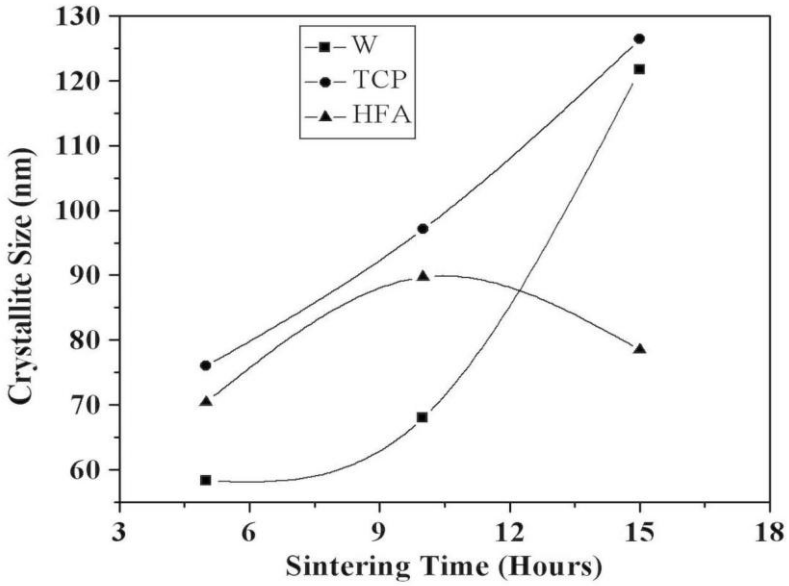

Fig 4. Variation of Crystallite Sizes with Sintering Time Interval

Fig 5 shows the variation of diameter shrinkage and diameter shrinkage time co-efficient (α) of the glass ceramics samples with the sintering time intervals. Gradients of the plots slightly decrease after 10 hours indicating a relative deceleration of densification process due to the crystallization which hinders sintering by obstructing the viscous flow of the particles thus decreasing the rate of densification in accordance with the fraction of unsintered substance. Fig. 6 shows the variation of bulk density with sintering time interval. Rise in bulk density (2.49 g/cm^3 to 2.73 g/cm^3) in sintering time interval 5-10 hours is greater than that (2.73 g/cm^3 to 2.88 g/cm^3) in domain 10-15 hours indicating a significant thickening process has already occurred in the former time interval in which substantial amount of grain boundaries movements and pores exclusions have taken place. This process of densification continues in the latter time interval domain as well but with a slower rate.

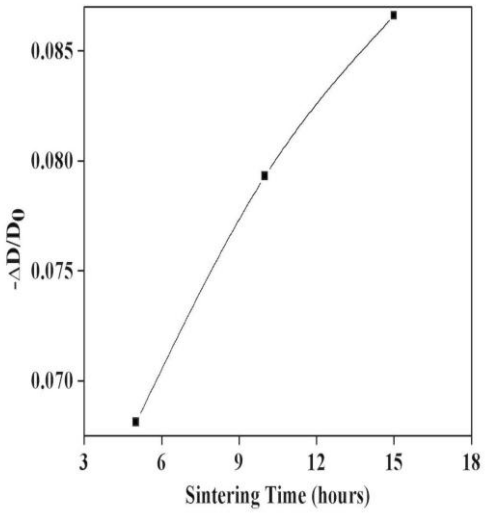

Fig 5a. Variation of Diameter Shrinkage with Sintering Time Interval

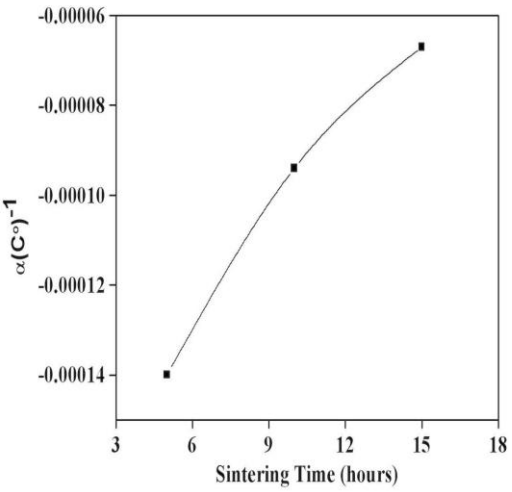

Fig. 5b. Variation of Diameter Shrinkage Co-efficient with Sintering Time Interval

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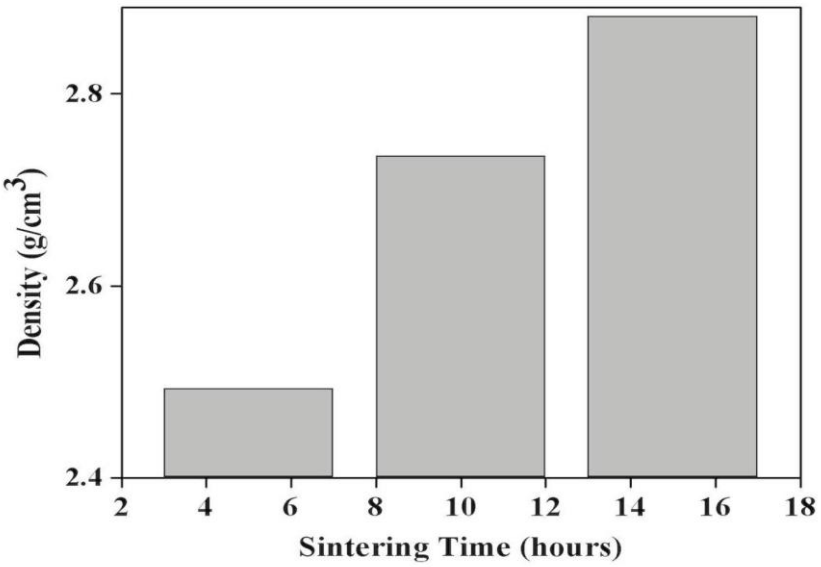

Fig 6. Variation of Bulk Density with Sintering Time Interval

SEM micrographs of glass ceramic samples GC_1, GC_2 and GC_3 are shown in Fig 7a, 7b and 7c respectively. The grains are of different sizes and asymmetrical shapes. Sample GC_1 has visible porosity in its matrix which is lessened in GC_2 due to the densification process during sintering. The diffusion process of the materials along the grain boundaries speeds up at higher sintering time intervals and vacancies travel in opposite direction towards the surface of the material where they are annihilated. Thus coalescence of agglomerates occur beginning with the formation of necks and so process of densification continues. The increased density and coalescence of grains are much prominent in GC_3 where the pores have eliminated to much extent. This increase in densification and reduction in porosity are in agreement with the diameter shrinkage coefficient and bulk density plots. The average grain size increases with the increased sintering time; it is 20 μm, 40 μm and 55 μm for GC_1, GC_2 and GC_3 respectively as shown in fig. 8.

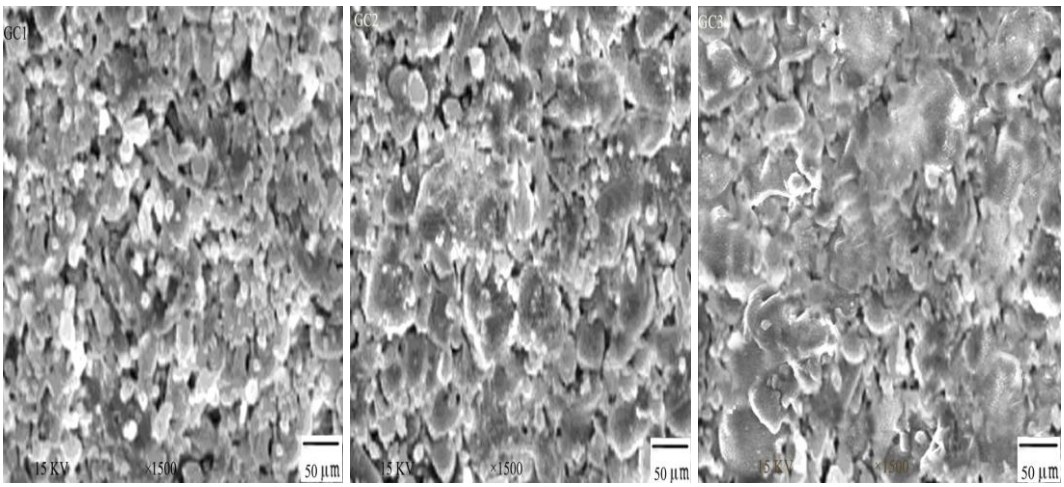

Fig 7a. SEM of GC1 **Fig 7 b. SEM of GC2** **Fig 7 c. SEM of GC3**

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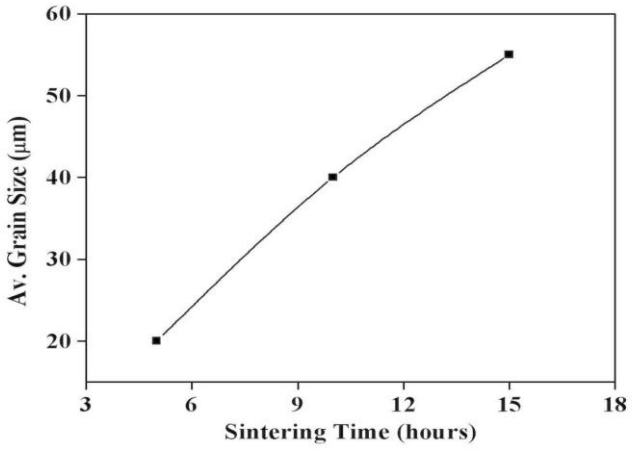

Fig. 8: Variation of grain size vs sintering time

B. Biocompatibility

After immersion of the samples (GC1, GC2 and GC3) in the simulated body fluid for 30 days at room temperature, EDS (Figs. 9a, 9b and 9c) confirms the bioactivity of all the samples by showing the existence of Carbon along with Ca and P which corresponds to formation of Hydroxycarbonate Apatite, a bioactive phase that is essential for the formation of a bond with the tissues and its rate of formation establishes the degree of bioactivity [2,3]. Formation of HCA in the physiological environment may be explained by a series of surface reactions [23] involving exchanges of Na^+ or Ca^{2+} ions with H^+ or H_3O^+ ions from the solution at the material surface, formation of silanols (Si-OH) at the material solution interface, migration of Ca^{2+} and PO_4^{3-} ions to the surface through the SiO_2 rich layer, formation of calcium phosphate layer and crystallization of HCA by incorporating CO_3^{-2} ions and reveals the highest bioactivity of GC2 that is confirmed by FTIR (fig. 10).

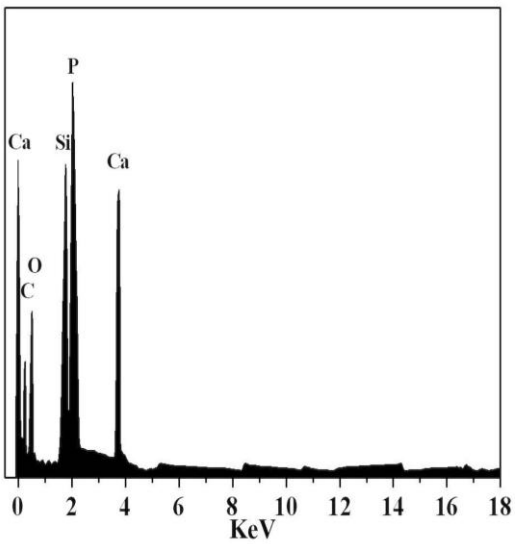

Fig 9 a. EDS spectrograph of GC1 after immersion in SBF

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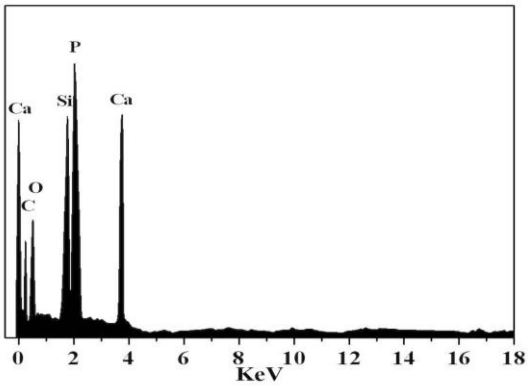

Fig 9 b. EDS spectrograph of GC2 after immersion in SBF

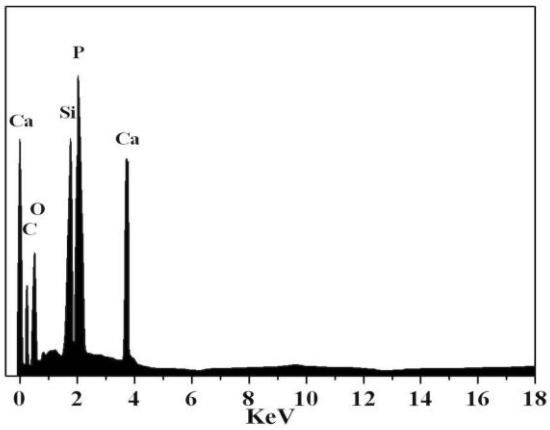

Fig 9c. EDS spectrograph of GC3 after immersion in SBF

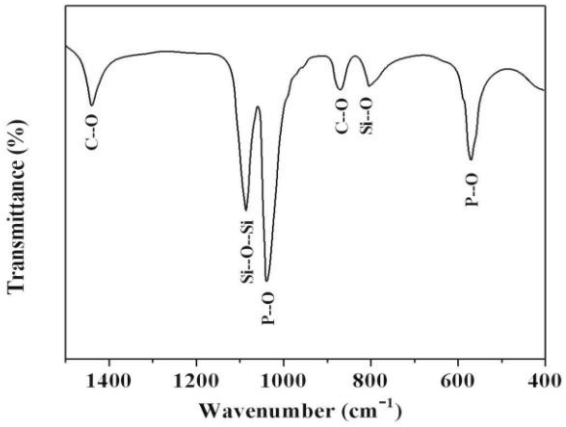

Fig. 10. FTIR plots of sample GC_2 after immersion in SBF

The FTIR graph of GC2 shows some absorption of infrared radiations at wave numbers 1440 cm^{-1} and 871 cm^{-1} due to $C\text{-}O_{(stretch)}$ type of molecular vibrations that corresponds to the formation of Hydroxy Carbonate apatite

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(HCA) layer on the surface of sample in simulated body fluid suggesting that the glass ceramics material under investigation that is sintered at 1000 C° for 10 hours is highly bioactive.

IV. CONCLUSION

Glass of the composition (% wt) ($34SiO_2$-$46CaO$-$14.5P_2O_5$-$4Na_2O$-$1CaF_2$-$.5MgF_2$) was prepared by simply melting the mixture and then quenching the melt in water. Sintering was carried out at 1000 C° for three different time intervals 5h, 10h and 15 hours respectively. The main crystalline phases formed after controlled heat-treatment of the glass were Hydroxyfluoroapatite (HFA), Tricalcium phosphate (TCP) and Wollastonite (W) respectively as conformed by the X-ray Diffraction (XRD). Bulk properties of the glass ceramic samples were examined by studying the density and diameter shrinkage after respective heat treatments. Structural characterization illustrated that the rate of densification was higher for 5-10 hours sintering time interval domain than that for 10-15 hours domain due to the already achieved densification in the former time interval. Crystallite and grain sizes also increased accordingly. At 15 hours sintering time interval, decomposition of HFA into TCP and W was also observed. The samples were immersed in SBF for 30 days at ambient temperature. FTIR and EDX revealed the presence of HCA phase showing that the glass ceramics under investigation, prepared at sintering temperature of 1000°C for 10 hours was more bioactive.

V. ACKNOWLEDGEMNT

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