

Role of Ga_2O_3 ions on the structural and bioactive behaviour of $\text{B}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-CaO}$ glass system

G. Jagan Mohini, N. Krishnamacharyulu, G. Sahaya Baskaran, N. Veeraiah

Abstract— A multi component glasses of the composition of $43\text{B}_2\text{O}_3\text{-}5\text{SiO}_2\text{-}2\text{P}_2\text{O}_5\text{-}20\text{Na}_2\text{O}\text{-}(30\text{-}x)\text{CaO}\text{:}x\text{Ga}_2\text{O}_3$ (x between 0 to 3 in steps of 0.5) were synthesized, by melt quenching technique and their bioactivity was investigated as a function of Ga_2O_3 concentration. Structural variations of the glasses were analyzed using optical absorption and infrared spectra of the samples. For understanding the bioactivity, the samples were immersed in simulated body fluid (SBF) solution for prolonged times (~ 30 days) and the weight loss measurements were carried out. The spectroscopic studies were repeated on the post immersed samples. From the comparison of the analysis of the spectroscopic data of both pre-immersed and post-immersed samples together with the information on variation of pH value of residual solution as a function of immersion time, it is concluded that the participation of gallium ions in tetrahedral positions is hindrance for the formation of HA layer and for the bioactivity of the samples..

Index Terms— Gallium ions, Spectroscopic studies; Bioactivity, $\text{B}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-CaO}$ glass system.

I. INTRODUCTION

Bioactive glasses are a class of biomaterials that have been used clinically as hard tissue regenerative materials in dental and orthopedic surgeries. These glasses, when exposed to physiological solutions, are able to form an amorphous calcium phosphate layer on their surfaces, this layer crystallizes into a biologically active hydroxyl carbonate apatite layer (HAP) within a few days. This phase is chemically and structurally equivalent to the mineral phase in bone and is responsible for the interfacial bonding [1]. Bioactive glasses show the ability to bond to bone tissue. Since the discovery of 45S5 bioglass many artificial biomaterials based on Hench's glasses have been developed and successfully employed in clinical applications for repairing and replacing parts of the human body. By varying the chemical nature and the concentrations of chemical constituents new important biological properties can also be added and the glass can be tailored to specific clinical applications. Recently, the researchers have concentrated on borate based bioactive glasses as they seem to exhibit bioactivity. However, some borate based bioactive glasses

degrade faster because of their lower chemical durability. In order to overcome the mismatch between the degradation rate and growth rate of new bone, it is necessary to manipulate the composition of these glasses.

Besides this, borate based bioactive glasses seems to support tissue infiltration *in vivo*, as well as cell proliferation and differentiation *in vitro*. In bone tissue engineering applications it is necessary to enhance the generation and growth of hydroxyl apatite on the surface of bioactive glasses in a certain reaction time in body environment [2]. The addition of Ga_2O_3 to the base glasses enhance the glass forming ability with improving IR transmission [3]. A vast number of diversified studies, that include X-Ray and neutron diffraction, IR, Raman, XPS and NMR, on Ga_2O_3 containing glasses, have revealed that Ga^{3+} ions exist mainly in four-fold coordination. Nevertheless, quite often, the gallium ions do exist in glass networks with three fold oxygen atoms for the sake of charge balance. The modifier oxides play a major role in maintaining the gallium ions in four-fold coordination [4].

Further, Gallium play a vital role in normal physiological function related to bone metabolism [5–6]. It was reported that gallium protects the HAP matrix, improving the bio mechanical properties of skeletal system [7–8]. Keeping in mind the positive qualities of this element, this paper is devoted to study the structural role of gallium ions in improving the bioactive properties $\text{B}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-CaO} : \text{Ga}_2\text{O}_3$ glasses

Thus the objective of the present study is to synthesize bioactive glass with B_2O_3 , SiO_2 , P_2O_5 , Na_2O , CaO and Ga_2O_3 as the constituents, to obtain the structural information from the MIR and optical absorption spectra, to study the influence of Ga_2O_3 on the degradability of the glass in SBF solution by measuring its weight loss and variations in pH value of the SBF solution as a function of Ga_2O_3 .

II. MATERIALS AND METHODS

The details of the chemical composition of the glasses chosen for the present study are furnished in Table 1. Required amounts of analytical grade powders of reagents SiO_2 , H_3BO_3 , P_2O_5 , CaCO_3 , Na_2CO_3 and Ga_2O_3 were taken and thoroughly mixed in an agate mortar with pestle. Then the charge taken in silica crucible was placed in a pre-heated automatic temperature controlled electrical furnace for 30 min. which is at 1050°C . The melt was poured in a brass mould and immediately shifted to muffle furnace for annealing purpose which was at 400°C to avoid thermal shock. The samples were then grounded and optically polished.

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The density of the glasses before and after immersion was measured by the standard Archimedes' principle using deionized water as buoyant liquid to an

Table 1

Details of the chemical composition of the glasses in mol%

Glass code	B ₂ O ₃	SiO ₂	P ₂ O ₅	CaO	Na ₂ O	Ga ₂ O ₃
G ₀	43	5	2	30	20	0
G ₅	43	5	2	29.5	20	0.5
G ₁₀	43	5	2	29	20	1
G ₁₅	43	5	2	28.5	20	1.5
G ₂₀	43	5	2	28	20	2
G ₃₀	43	5	2	27	20	3

accuracy of 0.0001g. with electrical digital balance (Shimadzu make AU Y 220 model). Infrared spectra of both the pre-soaked and post-soaked samples in SBF solution were recorded in transmission mode on a JASCO-FTIR-5300 spectrophotometer with a resolution of 0.1 cm⁻¹ in the range 400–4000 cm⁻¹ using KBr pellets. The optical absorption spectra of both sets of the samples were recorded at room temperature in the wavelength range 300–800 nm, using JASCO make V-670 UV-vis spectrophotometer with scanning speed of 200 nm/min. The X-ray diffraction analysis of the SBF reacted samples is performed using Bruker X D8 advance diffractometer at temperature 298 K°. The CuK_α radiation (λ= 1.54 Å) with nickel filter is used for the analysis over the range of 2θ= 20°-80° to confirm the formation of hydroxy apatite layer on the glass surface after soaking in simulated SBF solution. The reference data for the interpretation of XRD patterns is obtained from JCPDS diffraction card files. The scanning electron microscope (Tescan, Model VEGA3 LMU) is used to obtain surface image of glass samples to explore its surface morphology. The micrographs obtained using SEM studies helped to acquire the knowledge about the hydroxy apatite layer formed on the glass samples. The surfaces of the sample were coated with a thin layer of gold before the test because of the poor electrical conductivity of the glass.

Weight loss measurements were taken for all the glass samples. The dimensions of the glass samples were measured in order to calculate their surface area and then the initial weight was taken using electrical balance. The polished samples were placed in closed polyethylene containers which contain pre-calculated volume of SBF solution after cleaning them in acetone bath and were incubated at 36.5°C. The ratio between the surface area of the sample and volume of the solution (1:10) is maintained constant in all the cases in order to avoid defects resulting from volumetric differences. The samples were removed from their respective containers at various intervals of time and excess moisture was removed using tissue paper and reweighed. Then the pH value of SBF solution is measured with pH meter. Later on, the samples were placed back into the containers and were kept in incubator. The pH meter was calibrated with fresh standard buffered solution every time.

For *in vitro* studies, optically polished samples were placed in simulated body fluid solution and incubated at 36.5°C throughout the experiment to simulate a human physiological environment. The preparation of SBF was carried out according to the method proposed by Kokubo et al

[9]. The solution was buffered to pH 7.4 with Tris-buffer (hydroxyl methyl amino methane) and hydrochloric acid. After 30 days of immersion the glass pieces were taken out, washed with distilled water and dried in air. The surfaces of dried samples were analyzed by MIR, XRD, SEM and optical absorption techniques to detect apatite layer. In order to perform MIR test, the HAp powders were obtained by gently scratching the surfaces of the dried glass samples. With our naked eye inspection, it is clear that all the soaked samples were covered with a thin white layer

III. RESULTS

From the measured values of density *d* and calculated average molecular weight of the glasses, various physical parameters such as gallium ion concentration *N_i*, mean gallium ion separation *R_i*, polaron radius *R_p* and field strength *F_i* are evaluated using the conventional formulae [10] and are presented in Table 2.

Table 2

Summary of the data on various physical parameters of B₂O₃-SiO₂-P₂O₅-Na₂O-CaO:Ga₂O₃ glasses.

Property	G ₀	G ₅	G ₁₀	G ₁₅	G ₂₀	G ₃₀
Density before immersion (g/cm ³)	2.42	2.4335	2.44	2.45	2.46	2.47
Density after immersion (g/cm ³)	2.24	2.375	2.37	2.40	2.43	2.44
Avg. mol. wt.	64.99	65.65	66.3	66.9	67.6	68.9
Ga ion conc. <i>N_i</i> (10 ²² ions/cm ³)	-	1.1163	2.19	3.29	4.38	6.49
Inter ionic distance of Ga ions <i>R_i</i> (Å ⁰)	-	4.474	3.57	3.12	2.83	2.48
Field strength <i>F_i</i> (10 ¹⁵ /cm ²)	-	9.223	14.4	18.9	22.9	29.8

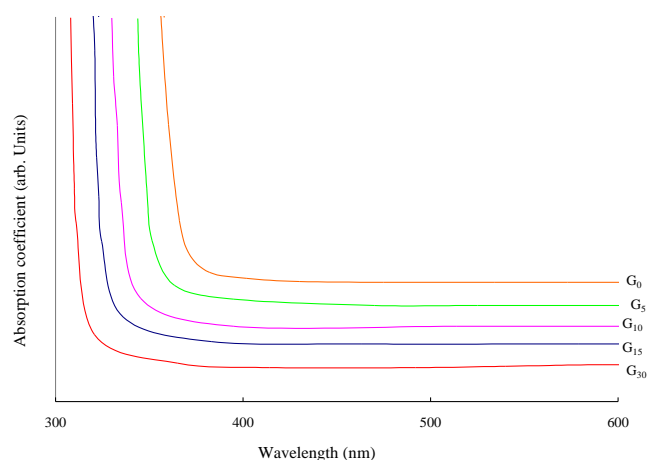


Fig. 1 Optical absorption plots for B₂O₃-SiO₂-P₂O₅-Na₂O-CaO:Ga₂O₃ Glasses

Density is known to be an important measure of the compactness or close packing of atoms in glass structures.

Therefore, density gives an indication of the degree of change in the glass structure with the change in the glass composition associated with the addition of metal oxide. In the present glasses, the contents of B₂O₃, SiO₂, P₂O₅ and Na₂O remain constant while the contents CaO is varied between 30–27 mol% and Ga₂O₃ between 0–3 mol%. The bulk glass density before immersion is found to be increasing gradually with incorporation of Ga₂O₃ content from 0.5– 3 mol % (Table 2). The increased density could be attributed to the replacement of the low density oxide CaO (3.34 g/cm³) with high density oxide Ga₂O₃ (6.44 g/cm³). Further, the densities of SBF treated samples are observed to decrease than those of pre-soaked samples.

The optical absorption spectra of (Fig. 1) B₂O₃–SiO₂–P₂O₅–Na₂O–CaO: Ga₂O₃ glasses were recorded at the room temperature in the wavelength region 300–800 nm. The absorption edge for glass G₀ was observed at 358 nm. The gradual addition of Ga₂O₃ from 0.5–3 mol% makes the absorption edge to shift towards shorter wavelength side (Table 3). From the observed absorption edges, we have evaluated the optical band gaps (E₀) of these glasses by drawing Tauc plots between (α h ω)^{1/2} and hω as per the equation:

$$\alpha(\omega) h \omega = C (h \omega - E_0)^2 \quad (1)$$

Table 3

Summary of data on optical absorption of B₂O₃– SiO₂– Na₂O– CaO: Ga₂O₃ glasses

Glass	Cut-off wavelength (nm)	Optical band gap E ₀ (eV)
G ₀	358	3
G ₅	343	3.1
G ₁₀	330	3.2
G ₁₅	321	3.3
G ₃₀	308	3.4

Table 4

Data on MIR band positions in (cm⁻¹) of B₂O₃–SiO₂–P₂O₅–Na₂O–CaO: Ga₂O₃ glasses before immersion in SBF solution

Vibrational .Groups	Glass G ₀	Glass G ₅	Glass G ₁₀	Glass G ₁₅	Glass G ₃₀
B–O stretching of BO ₃ Units	1520	1519	1519	1519	1520
Si– O– Si Stretching	1243	1243	1247	1245	1240
BO ₄ /PO ₄ ³⁻ Units	1018	1018	1020	1020	1020
B–O–B Linkages	714	714	713	711	712
GaO ₄ Units	-	611	619	617	619

Tauc plots are drawn for all the glasses in which considerable part of each curve is observed to be linear (Fig. 2). From the extrapolation of the linear portion of these curves, the value of

the optical band gaps (E₀) are determined; the optical band gaps are found to increase with the increase of Ga₂O₃ Content. (Table 3). Thus, the band gap maximum is observed for the sample G₃₀ among all the unsoaked samples indicating highest chemical durability.

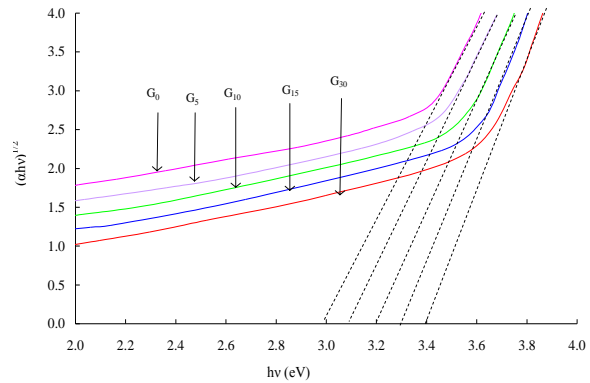


Fig. 2. Tauc plots for evaluating optical band gap of B₂O₃–SiO₂–P₂O₅–Na₂O–CaO: Ga₂O₃glasses

Fig. 3 shows the infrared spectra in mid-infrared region of all the samples recorded before immersion. The spectra of parent glass G₀ exhibited vibrational bands around 1520 cm⁻¹ (due to asymmetric stretching relaxation of the bond B–O of BO₃ units), 1019 cm⁻¹ (due to stretching vibration of BO₄ units/(PO₄)³⁻ units), 1243 cm⁻¹ (due to Si–O–Si stretching vibrations) and 714 cm⁻¹ (due to B–O–B linkages) [11, 12, 13]. With the introduction of Ga₂O₃ a new vibrational band at 611cm⁻¹ have been developed which could be assigned due to GaO₄ structural units [14] (Table 4). The intensity of vibrational bands corresponding to GaO₄ units and BO₄ units are observed to increase with increase in Ga₂O₃ content at the expense of BO₃ units. The intensity of Si–O–Si and B–O–B units are found to be decreasing with the increase in concentration of Ga₂O₃.

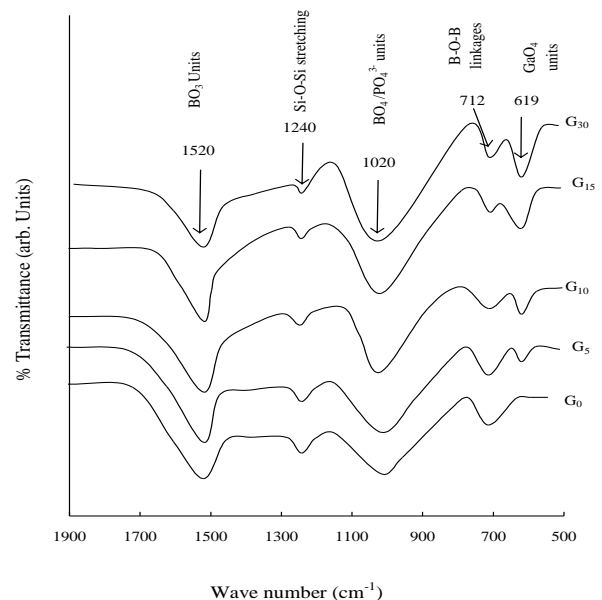


Fig. 3. MIR spectra of glasses B₂O₃–SiO₂– P₂O₅ – Na₂O–CaO: Ga₂O₃ before immersion in SBF solution.(The spectra are Y-shifted for the sake of clarity).

In the present study, the dissolution of the glass samples was studied in simulated body fluid with the primary idea of understanding the bioactive behaviour *in vitro*. In biomaterial

research, the *in vitro* studies involving dissolution experiments in solutions similar in composition to those present inside the human body (eg. simulated body fluid, SBF) have been recognized as preliminary screening tests on new candidate implant materials [15]. Fig. 4(a) shows the degradation presented as percentage of weight loss as a function of time for various Ga₂O₃ containing and the Ga₂O₃-free glasses. The degradation of the glasses increased with time for all the tested glass compositions and it is observed to be decreasing with the increase in concentration Ga₂O₃. Figure 4(b) shows that the increase in the pH value of the SBF solution versus immersion time followed a trend similar to that of the degradation studies of the glasses.

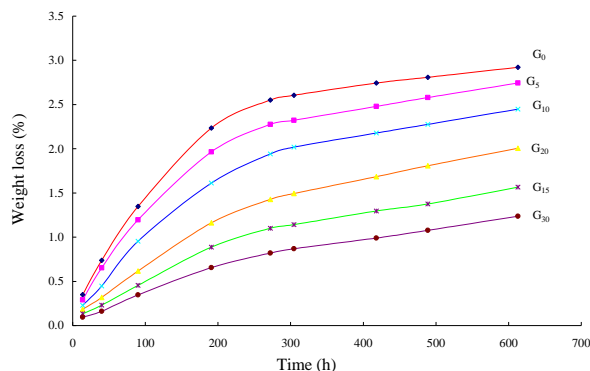


Fig.4(a) Percentage of weight loss vs dissolution time of B₂O₃-SiO₂-P₂O₅-Na₂O-CaO :Ga₂O₃ glasses during degradation in SBF solution maintained at 36.5°C

For understanding the structural variations in the samples due to immersion in SBF solution, optical absorption and infrared spectra of these glasses were repeated after soaking them in the SBF solution for about 30 days.

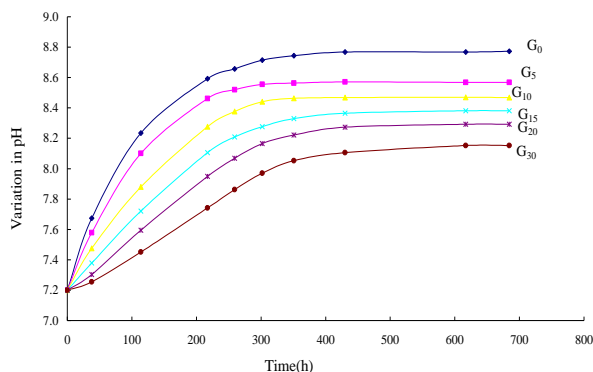


Fig. 4(b) Variation of pH of the SBF solution measured on various time intervals for the B₂O₃-SiO₂-P₂O₅-Na₂O-CaO:Ga₂O₃ glasses during immersion

The optical band gaps of all the studied samples before and after immersion are shown in Fig.5. These values give us some insight on layer formation on the surface of glasses. The layer formation on these surfaces involves several reactions such as glass dissolution and precipitation between the glass and SBF solution [16]. The change in chemical composition causes some structural changes on the glass surface which leads to change in band gap and optical transmission. The band gaps of all the studied samples decreased after soaking in SBF solution. The maximum change is observed for the glasses doped with higher concentration of Ga₂O₃.

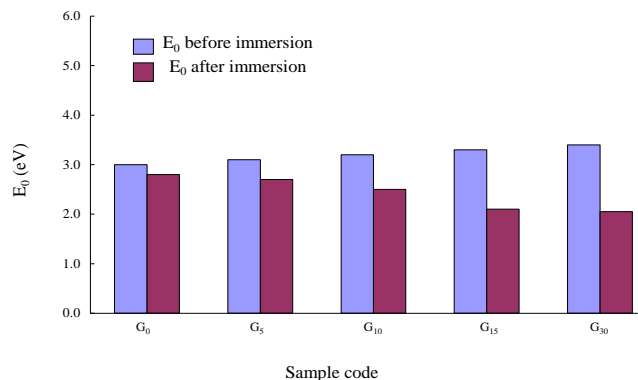


Fig.5 The optical band gap of the B₂O₃-SiO₂-P₂O₅-CaO-Na₂O:Ga₂O₃ glasses before and after immersion for 30 days.

In Fig. 6(a), the MIR spectra of layer formed on the surface of glasses after immersion in SBF solution were presented. The spectra are found to be different from that of unsoaked samples which are indicative of significant surface structural changes. For obtaining better inference, we have shown the spectra of glass G₁₅ in Fig. 6(b) before and after immersion. The comparison reveals that intensity of vibrational bands around 1020cm⁻¹ and 610 cm⁻¹ corresponding to PO₄³⁻/BO₄ and GaO₄ units respectively increased many folds with slight variation in band positions. Besides this, new bands at 1420 cm⁻¹ and 1635 cm⁻¹ corresponding to C-O stretching in carbonate groups substituted for phosphate groups in apatite lattice and HCO₃ units respectively have been developed. The vibrational bands at 1520 cm⁻¹, 710 cm⁻¹ and 1243 cm⁻¹ corresponding to BO₃ units, B-O-B linkages and Si-O-Si stretching vibrations could not be resolved in post-soaked MIR spectra. The presence of vibrational band at 3438 cm⁻¹ could be attributed to stretching mode of O-H group [17]. The close observation of MIR spectra of post immersed samples further indicated a gradual decrease of intensity of bands corresponding to phosphate and carbonate groups with increase in the content of Fig. 7 shows the XRD patterns of studied glass samples after soaking in SBF solution for 30 days. The broad peaks observed at 2θ=30.672 and 46.584 reflect the presence of (211) and (222) atomic planes (JCPDS card no 09-432). Generally, the broad peaks in XRD pattern indicate amorphous nature. But, formation of HCA layer on the surface of SBF treated samples is evident from MIR spectra of post-soaked samples. This situation can be explained with the aid of some reports which states that the observed broadening may be an indication of formed HA layer was poorly crystallized or the size of HA crystallite is on a nano metre scale or the combination of both. In fact, according to the studies of J.P. LeGeros et al, in order to obtain X-ray diffraction maxima of an apatite phase, its crystals must contain more than 20 unit cells. Below this value, an XRD study of such an apatite phase would conclude that the material is amorphous.

Fig. 8 Shows the SEM image of the surface of the SBF treated G₃₀ glass specimen. SEM analysis of glasses treated in SBF yield information about changes in surface morphology. The micrographs were recorded with 500x magnification. These pictures provided visual evidence of the formation of a surface layer on the glasses. Some grain-like growths of different sizes have been appeared on the surface of the specimen, which can now be presumed to be apatite crystals as identified by FTIR technique.

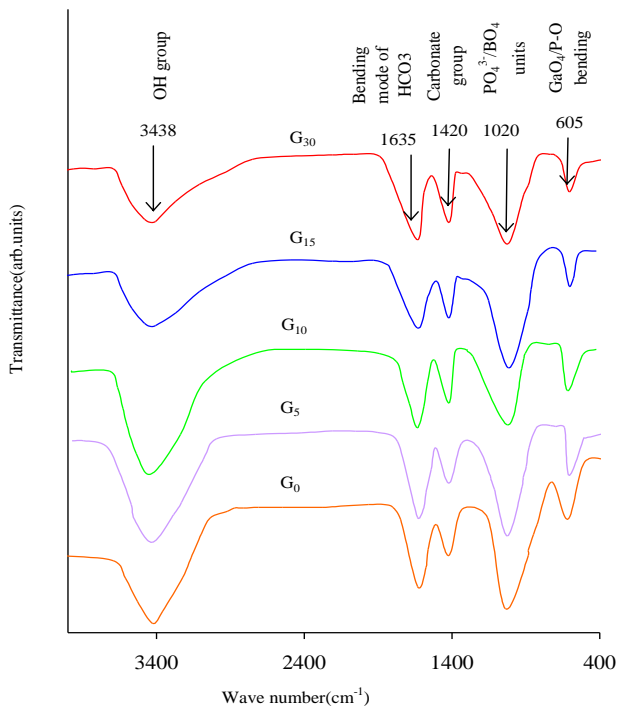


Fig. 6(a). MIR transmission spectra of $B_2O_3-SiO_2-P_2O_5-Na_2O-CaO:Ga_2O_3$ glasses soaked in SBF for 30 days

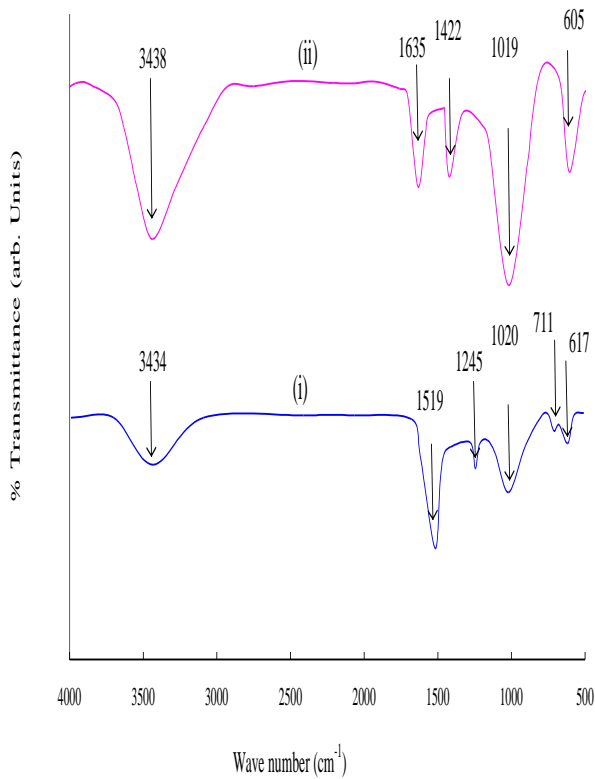


Fig. 6(b). MIR spectra of the glass sample G_{15} (i) before immersion (ii) after immersion in SBF solution for 30 days

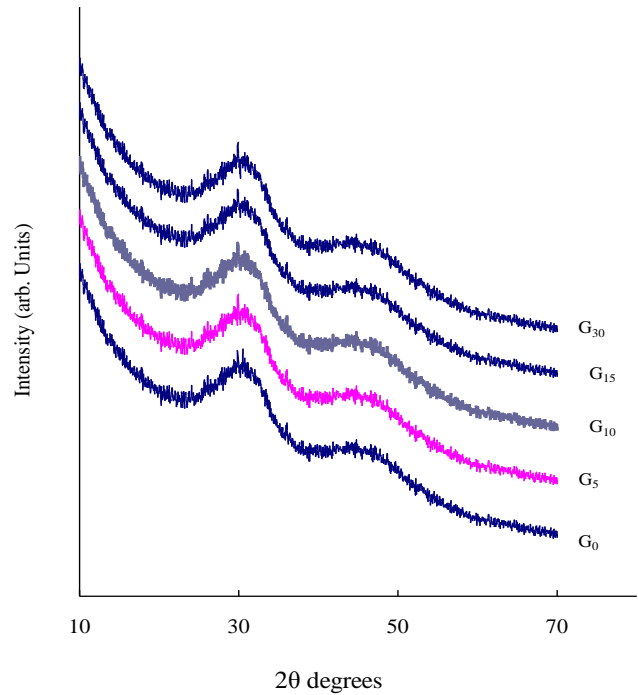
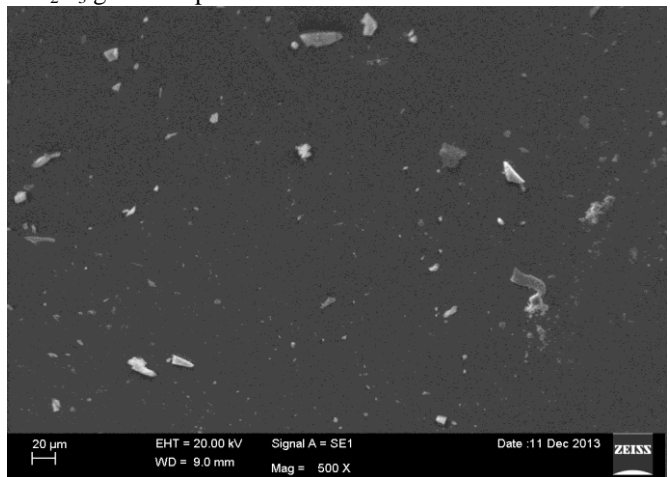


Fig. 7. XRD patterns of $B_2O_3-SiO_2-P_2O_5-Na_2O-CaO:Ga_2O_3$ glass samples after immersion in SBF Solution for 30



days

Fig. 8 SEM micrograph of G_{30} sample after soaking in SBF for 30 days

IV. DISCUSSION

The HAp layer formation involves several chemical reactions between the glass/liquid interfaces. This is evident from the studies of MIR, XRD and optical studies.

The composition of the chosen glass system is an admixture of the glass formers, modifiers and intermediates. Borate glasses are very interesting materials because of their rich chemistry. It can change easily its co-ordination with oxygen between three and four [18–19]. Besides this, boron has smallest mass compared to other network forming elements (Si, P and Ge). In earlier, it is assumed that the structure of B_2O_3 consists of boron-oxygen triangles (BO_3) [20–21]. Later, Krog-Moe [22] suggested that the structure of B_2O_3 consists of large concentration of an intermediate unit which is formed by joining three boron-oxygen triangles named as boroxol rings or boroxol

groups (B₃O₆). It is assumed that the addition of alkali oxide forces some of the borons to change from triangular to tetrahedral co-ordination without the formation of NBOs [23]. But according to Shelby [24], in addition to boroxol rings, alkali borate glasses contain a number of intermediate structural groups such as tetra borates, di-borates, penta-borates etc. Naturally the excess modifier oxide causes NBOs to form and the rest of borons remain in triangular co-ordination. Hence the studied glasses exhibit both BO₃ and BO₄ units and the reason for the formation of is the action of modifier oxides on the triangular boron.

SiO₂ is a popular glass former that participates in the glass network with tetrahedral [SiO_{4/2}]⁰ units and all the four oxygens in SiO₄ tetrahedron are shared. The Si-O linkages normally are broken by the addition of modifiers like Na₂O and CaO. The depolymerization results in the formation of metasilicates, pyrosilicates and orthosilicates in the order: [SiO_{4/2}]⁰, [SiO_{3/2}O]⁻, [SiO_{2/2}O₂]²⁻, [SiO_{1/2}O₃]³⁻, and [SiO₄]⁴⁻ which are designated as Q⁴, Q³, Q², Q¹, and Q⁰, respectively [25]. The presence of such SiO₄ units is evident from MIR spectra of these glasses.

Both Na₂O and CaO act as modifiers; generally, Na⁺ and Ca²⁺ ions occupy the interstitial positions while the oxygens of these oxides break the local symmetry and introduce co-ordinate defects known as dangling bonds along with non-bridging oxygens (NBO) [26]

P₂O₅ is, yet, another strong glass former that participates in the glass network in the form of PO₄ structural units. The PO₄ tetrahedra are linked together with covalent bonding in chains or rings by bridging oxygens [27].

Ga₂O₃ is considered to act as network former, if Ga³⁺ ions take preferentially four fold coordination in oxide glasses. The excess negative charge on GaO₄ tetrahedra are compensated either by localization of a modifier near by or by generation of three fold oxygens. The GaO₄ tetrahedrons may enter the glass network and alternate with BO₄ tetrahedrons. In some glass networks, the Ga ions are also found to be in modifier position with GaO₆ structural units [28].

Thus, from the discussions based on the literature and the analysis of the results IR spectral studies, one can conclude that B₂O₃-SiO₂-P₂O₅-Na₂O-CaO;Ga₂O₃ glass network is composed of BO₃ units, BO₄ units, PO₄³⁻ units, Si-O structural units and gallium ions in tetrahedral positions. From MIR studies, it may be concluded that the addition of Ga₂O₃ causes the strengthening of glass matrix. This result is consistent with the result observed from optical study.

The gradual increase of tetrahedrally coordinated gallium ions with increase in the Ga₂O₃ content (up to 3 mol%) may cause to shift the absorption edge towards the shorter wave length side. Thus, the lower the concentration of octahedral Ga³⁺ ions, lower is the concentration of NBOs in the glass matrix. This leads to decrease in the localization of electrons, thereby decreasing in the donor centers in the glass matrix. The presence of smaller concentration of these donor centers increases the optical band gap and shifts the absorption edge towards shorter wavelength side as observed [12].

The degradation of the borate-based glass in the SBF solution is accompanied by the release of the glass modifiers such as Na, Ca and the conversion of the glass to a hydroxyapatite-type material. Because of the high solubility

of sodium hydroxide, the Na⁺ ions dissolved from the glass should remain as soluble ions in the SBF solution and Ga₂O₃ in aqueous environment forms insoluble Ga(OH)₃, which dissolves partially for pH>7. On the other hand, hydroxyapatite, Ca₅(PO₄)₃(OH), the most stable calcium phosphate phase in aqueous solution at pH >4-4.5, has a low solubility product at room temperature ($K_{SP} = 2.35 \times 10^{-59}$), so the Ca²⁺ ions are incorporated in the precipitated hydroxyapatite-type material. Further, the data obtained revealed that the weight loss is decreasing with increase in the content of Ga₂O₃. Thus the degradation indicates that most of Ga³⁺ ions occupy tetrahedral (GaO₄) positions and alter the BO₄ units and forms B-O-Ga bonds that leads to increase in the rigidity of the network and makes the glass dissolution more difficult. This result is consistent with the result obtained from the optical study.

After immersion of the glass samples, the pH of the SBF solution varies as a result of the reactions occurring at the solid/liquid interface [29]. The rapid rise in pH in initial stages suggests the more noticeable changes have occurred in the earliest immersion period. Moreover, the continuous increase in pH may be attributed to the continuous glass dissolution in the SBF solution which is supported by the curves of % weight loss. In the degradation of the borate-based glass and its conversion to a hydroxyapatite-type material in the SBF solution, borate ions are released into the solution, while phosphate ions are consumed from the solution. Since boric acid is weaker than phosphoric acid, this process coupled with the release of Na⁺ ions from the glass leads to an increase in the pH of the solution. The data obtained gives an idea about the environment produced by the implants in active system.

Since the degradation of the borate-based glasses and the conversion to form a hydroxyapatite-type material are controlled by essentially the same reactions, the conversion kinetics of the glass should show a trend similar to those for the weight loss and the pH of the SBF solution. The similar trends observed in the weight loss and pH variation of the SBF solution show that this was indeed so.

The decrease in the band gap after immersion may be attributed to the formation of crystalline HA layer on the surface of these samples reduces the porosity and increases the ordering which leads to decrease in the optical band gap [30,17].

The increase in the intensity of vibrational bands around 1020cm⁻¹ and 610 cm⁻¹ corresponding to PO₄³⁻/ BO₄ and GaO₄ units respectively may be inferred as follows: after immersion in SBF solution, the vibrational bands corresponding to phosphate groups are supposed to be overlap on these bands [31]. In addition, the growth of new band at 1420 cm⁻¹ corresponding to carbonate species signifies the incorporation of CO₃²⁻ ions in apatite lattice. Thus, the presence phosphate groups along with carbonate species confirm the formation of HCA layer on the glass surfaces. The close observation of MIR spectra of post immersed samples further indicated, a gradual decrease in the intensity of bands corresponding to phosphate and carbonate groups with increase in the content of Ga₂O₃. Thus, it may be concluded that bioactivity gradually decreasing with increase in Gallium content.

The ions BO₃³⁻, Na⁺, Ca²⁺ and PO₄³⁻ release from the glass into the leaching solution [30]. Besides this, Si-OH groups will be formed on the glass surface due to ion exchange

process or the attack of water molecules in SBF on Si–O–Si bonds [32]. Basically dissolution of Ca^{2+} , Na^{+} ions from the glass accelerates apatite nucleation by increasing the ionic activity product of apatite in the fluid. The hydrated silica formed on the surface provides sites for apatite nucleation. Once the apatite nuclei are formed, they grow spontaneously by combining with calcium and phosphate ions from the surrounding fluid [17].

V. CONCLUSION

Bioactive glasses viz., B_2O_3 – SiO_2 – P_2O_5 – Na_2O – CaO with variable concentration of Ga_2O_3 , were prepared. Optical absorption and MIR spectra analysis are carried out on the samples and it is established that increasing content of Ga_2O_3 (upto 3.0 mol %) in the glass system makes most of the Ga^{3+} ions to occupy tetrahedral (GaO_4) positions and enhance the polymerization of the network. The degradation studies show a fall in degradation of the samples immersed in SBF solution with the increase in the concentration of Ga_2O_3 . The structural inference obtained earlier is positively correlated with the degradation studies. The bioactivity of these glasses was studied *in vitro* in SBF solution. The post-soaked samples were analyzed using XRD, SEM and MIR for the formation of HAP layer. It is found that addition of Ga_2O_3 in higher concentration in the chosen glass system reduces the HAP layer formation on the glass surfaces. The present study reveals that higher is the concentration of tetrahedral Ga^{3+} ions (GaO_4 units) lower is the bioactivity and thus Ga^{3+} ions seems to inhibit the bioactivity.

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