Infrared absorption spectroscopy of some bio-glasses before and after immersion in various solutions

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The infrared absorption spectra of some selected bioglasses were investigated. By using powdered samples of the bioglasses, detailed infrared absorption spectra were generated over the 4000-200 cm\(^{-1}\) range, both before and after the glass powder were immersed in the studied solutions for 1 hr at 95°C. The absorption spectra differed with the bioglass composition and with the type of the leaching solution. Characteristic absorption bands due to vibrations of BO\(_3\), BO\(_4\), ALO\(_2\), MgO, or ZnO groups could be separately identified or combined as composite bands with that due to silicate chains. The Si-O non-bridging stretching band at ~950 cm\(^{-1}\) in the mid region and a far infrared band at ~280 cm\(^{-1}\) due possibly to Na cations vibration were the bands most sensitive to immersion hydration process. Changes were also seen in the appearance of absorption bands at ~1320, ~1460 and ~1640 cm\(^{-1}\) which could be attributed to phosphate, carbonate and water, respectively.

1 Introduction

It has been shown that certain compositions of glasses and glass-ceramics can bond to bone\(^6\). These materials have become known as bioactive ceramics. Some even more specialized compositions of bioactive glasses will bond to soft tissues as well as bone\(^6\). A common characteristic of bioactive glasses and bioactive ceramics is a time-dependent, kinetic modification of the surface that occurs upon implantation\(^5\).

The surface forms a biologically active hydroxy-carbonate apatite (HCA) layer which provides the bonding interface with tissues. The HCA phase that forms on bioactive implants is equivalent chemically and structurally to the mineral phase in bone. It is that equivalence which is responsible for interfacial bonding.

It is of utmost importance to follow up the mechanism and sequence of this surface calcium phosphate layer formation on bioglasses and bioglass-ceramics. Several analytical techniques were adopted to characterize these biomaterials.

Fourier transform infrared spectroscopy (FTIR) is a widely used technique that is routinely applied in this task. However, preparing samples of biomaterials for this investigation is often a tedious process. The main sampling problem in FTIR characterization of biomaterials is that nearly all solid materials are too opaque in their normal forms for direct transmission analysis in the mid-infrared region. The problem can be solved by reducing the optical density of samples to a suitable level by employing various sampling technique\(^8\). These procedures, however, can alter the nature of the sample and are time-consuming.

Various alternative techniques, such as diffuse reflectance (DRIFT) and attenuated total reflectance (ATR) can be employed, but are limited in applications due to stringent surface requirements and are not effective much above 1200 cm\(^{-1}\) and therefore does not pick up the silanol (SiOH) and water bands at the higher wave numbers. A reflectance spectrum can be extended to higher wave numbers only by a mathematical deconvolution (Kramers-Kronig analysis) in which the reflectance spectrum is converted to an absorption spectrum\(^9\). Other drawbacks of infrared reflectance spectra are that it is limited to surface depths of about 0.5 \(\mu m\) and that is affected by any surface roughening which may occur during corrosion. Photo-acoustic FTIR spectroscopy was also employed to characterize by hydroxyapatite of different origins\(^10\).

Recently, infrared absorption spectroscopy using the KBr techniques was fruitfully performed to study the structure-composition relation in various glasses and glass-ceramics\(^6\) and also to
follow up the effect of fast neutrons or gamma-rays radiation on the coherence of the glass network.

In this work, infrared absorption spectra were measured and compared for some selected bioglasses before and after immersion in various solutions to follow up the formation of the silanol (SiOH) groups and the calcium phosphate-rich layer. The immersion process was undertaken using powdered bioglasses which were immediately after careful drying used directly with pulverized KBr to prepare the required disc without disturbing their surfaces.

Another aim of this work is to investigate the variations in the internal structural groupings upon the substitution of 5% SiO₂ by B₂O₃, Al₂O₃, MgO or ZnO of the base bioglass.

2 Materials and Experimental Details

2.1 Preparation of bioglasses

All the chemicals used were of guaranteed grade and were used without further purification. The compositions of the studied selected bioglasses are shown in Table I. The materials used include fine-grained quartz for silica. Lime, magnesia and soda were introduced in the form of their respective anhydrous carbonates. P.O. was added in the form of ammonium hydrogen phosphate. Boric oxide was introduced in the form of orthoboric acid H₃BO₃. Alumina, CaF₂ and ZnO were added as such. The calculated batches were melted in platinum 2% Rh crucibles for 2 hr. The melting was carried out at 1400 ± 5.0°C. The homogenized melts were cast in a preheated stainless steel mold of the dimensions 1, 1, 1 cm.

The prepared bioglass samples were annealed at the appropriate temperature in a regulated muffle furnace adjusted at about 450°C. The muffle furnace was left to cool to room temperature at a rate of 20°C/hr.

2.2 Infrared absorption measurements

The infrared absorption spectra of the bioglasses were measured at room temperature (~20°C) in the range 200-4000 cm⁻¹ by a computerized infrared spectrophotometer type Jasco FT/IR-300E spectrometer using the KBr technique. The studied bioglasses were investigated as fine particles (< 0.3 mm in grain diameter) which were mixed with pulverized KBr in the ratio 0.002:0.2 (g glass powder to KBr respectively). The weighed mixture was then subjected to a pressure of 5 tons/cm² to produce clear homogeneous discs. The absorption spectra were measured immediately after preparing the desired discs. The same procedure was repeated for each bioglass after immersing of the bioglass powder in one of the following leaching solution: 0.5 gm of the glass powder was weighed in a sintered glass crucible G 4 Jena type. The sintered glass crucible containing the bioglass was placed into a polyethylene beaker (250 ml). 150 ml of the leach solution was introduced to cover the bioglass powder and the rest of the solution was placed into the beaker. The beaker was then covered with a polyethylene lid and placed in a regulated water bath at 95°C for 1 hr. After this time, the sintered glass crucible was fitted on a suction pump and the whole solution was pumped through it. The sintered glass crucible was transferred to an air oven at 120°C for 1 hr. Then the sintered glass crucible was put in a dessicator until cooled. The powdered bioglass was then ready for the preparation of the infrared measurement by the KBr technique. The following solutions were used in this work:

- 1-0.1 M hydrochloric acid solution (HCl);
- 2-0.1 M sodium hydroxide solution (NaOH);
- 3-1 M sodium bicarbonate solution (NaHCO₃);
- 4-0.5 M sodium phosphate solution (Na₃PO₄);
- 5-1 M sodium phosphate solution (Na₂PO₄);
- 6-Tris buffer (Tris(hydroxymethyl)aminomethane) + HCl (pH 7.4) and 7-Simulated Body Fluid (SBF) + HCl (pH 7.3).

3 Results

3.1 Infrared absorption spectra of bioglasses before immersion in solutions

The infrared absorption spectral curves of the bioglasses are shown in Figs 1-5 which reveal the following characteristics:

(1) The absorption spectra of the studied bioglasses resemble in general features the same absorption spectra usually observed from the traditional soda lime silica glasses.

(2) Fig. 1 shows the absorption spectrum of the base bioglass studied of the chemical composition SiO₂ 45%, Na₂O 24.5, CaO 24.5, P₂O₅ 6% together with the absorption spectra of the two bioglasses No. 2 & 3 in which boric oxide was introduced in substitution of 5% and 15% SiO₂ respectively. The principal absorption frequencies of the base bioglass
Fig. 1 — Infrared absorption spectra of bio-glasses:

1) 45 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 6 wt% P₂O₅;
2) 40 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 6 wt% P₂O₅, B₂O₃ = 5 wt% SiO₂; and
3) 30 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 6 wt% P₂O₅, B₂O₃ = 15 wt% SiO₂.

can be classified to occur in three regions. The mid
region extending from 2000–4000 cm⁻¹. The near-
infrared region extends from 2000–4000 cm⁻¹. The
far-infrared region extends from 100–400 cm⁻¹ and is
characterized by the presence of sharp and narrow
consecutive peaks belonging to vibrations of
network modifier cations. Curve No. (1) shows the
three broad well-defined bands at about 480, 950,
1060 together with two small bands at about 740
and 1550 cm⁻¹ and a shoulder at about 600 cm⁻¹. Also
it can be visualized the broad near-infrared band
with a maximum at about 3550 cm⁻¹ and a shoulder
at ~ 3430 cm⁻¹.

Curve (2) reveals the absorption spectra of the
bioglass No. 2 containing 5% B₂O₃. The spectra are
characterized by the development of the mid-
absorption to highly resolved composite bands with several peaks together with the appearance of an additional new sharp absorption band at 1400 cm⁻¹. Also the mid infrared absorption spectra reveal the shifting of their maxima to shorter wavenumbers. Curve (3) illustrates the absorption spectra of the bioglass No. (3) containing 15% B₂O₃ which reveal the same characteristic features observed with glass No. (2) but the maxima of the absorption bands are shifted to longer wavenumbers together with the appearance of an additional new small peak at ~1600 cm⁻¹.

(3) Fig. 2 illustrates the absorption spectra of both the base bioglass No. 1 together with bioglass No. 4 containing 5% Al₂O₃. The comparison of the two spectra reveals that the mid-absorption bands move to shorter wavenumbers. The absorption band at ~900 becomes more prominent approaching the intensity of the band at ~1050 cm⁻¹ which shifts to ~1020 cm⁻¹. A small band is observed at ~1450 cm⁻¹. The absorption band at 480-500 cm⁻¹ moves to about 450-460 cm⁻¹. In the far-infrared sharp bands, the band at ~400 cm⁻¹ is highly diminished while a sharp peak is clearly observed at ~250 cm⁻¹. The near infrared band becomes less intense.

(4) Fig. 3 reveals the absorption spectra of both base bioglass No. 1 together with bioglass No. 5 containing 5% MgO. The comparison of the two mentioned spectra reveal that the positions of the mid-absorption spectra shift to shorter wavenumbers and the bands are observed to be prominent and highly resolved into several component peaks. Also it can be visualized the appearance of two small absorption bands at about 1480 cm⁻¹ and about 1650 cm⁻¹. In the far-infrared region, the band observed in the base glass at ~400 cm⁻¹ is not clearly identified while a sharp narrow peak is observed at ~250 cm⁻¹. The near-infrared broad band centered at ~3600 cm⁻¹ remains prominent and shifts to higher wave number to ~3650 cm⁻¹.

(5) Fig. 4 shows the absorption spectra of both base bioglass No. 1 together with bioglass No. 6 containing 5% ZnO. The observed spectra illustrate the intensification of the mid-infrared absorption bands accompanied with the marked shift of the band positions to shorter wavenumbers. Two prominent bands centered at about 770 and 1480 cm⁻¹ are highly resolved. In the far-infrared region the sharp absorption band observed at ~400 cm⁻¹ in the base bioglass disappeared and is replaced by a
sharp narrow band at ~280 cm⁻¹. The near-infrared broad band at about 3600 cm⁻¹ remains prominent and its maximum moves to higher wavenumber at 3650 cm⁻¹.

(6) Fig. 5 reveals the absorption spectra of both the base bioglass No. 1 together with bioglass No. 7 containing CaF₂ 16%. The spectra show that the overall spectra are characterized by their low intensity and in the mid region two small peaks are observed at about 500 and 1020 cm⁻¹. Also the near-infrared band is observed at about 3600 cm⁻¹. Two small kinks can be hardly observed at about 1450 and 1550 cm⁻¹. No far-infrared bands can be observed.

3.2 Infrared absorption of bioglasses after immersion in selected solutions

The infrared absorption spectra of the studied bioglasses after immersion in the specified solutions are illustrated in Figs 6 to 12 which reveal the following characteristics:

Fig. 6 shows the infrared absorption spectra of the base bioglass (SiO₂ 45%, Na₂O 24.5%, CaO 24.5%, P₂O₅ 6%) before and after immersion in the selected solutions. Inspection of the absorption curves reveal that the main characteristic absorption bands are identified and only slight changes are observed which can be summarized as follows:

(a) On immersion of the base bioglass in HCl solution (0.1 M), the main mid-absorption band at ~1100 cm⁻¹ remains the same but slightly moves to higher wavenumber to ~1200 cm⁻¹ accompanied with the observation of a shoulder at about 1300 cm⁻¹. The neighbouring broad band at ~900 cm⁻¹ obviously decreases in intensity and is accompanied with the appearance of a small band at ~800 cm⁻¹. The near-infrared broad band at ~3650 cm⁻¹ is intensified. A peak at ~1640 cm⁻¹ is clearly resolved. The far-infrared sharp band with a highly resolved peak at about 300 cm⁻¹ remains but with slight shifting to longer wave number to 320 cm⁻¹. A new absorption kink is observed at about 1230 cm⁻¹.

(b) On immersion of the base bioglass No. (1) in either 0.1 M NaOH solution or 1 M Na₂PO₄ solution, the intensities of all the absorption bands are observed to decrease except the far-infrared band which retains the position and intensity as that before immersion.

![Fig. 3 — Infrared absorption spectra of bio-glasses:](image-url)

(1) 45 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 6 wt% P₂O₅; and
(5) 40 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 6 wt% P₂O₅, MgO = 5 wt% SiO₂.
Fig. 4 — Infrared absorption spectra of bio-glasses:
(1) 45 wt% SiO$_2$, 24.5 wt% CaO, 24.5 wt% Na$_2$O, 6 wt% P$_2$O$_5$, and
(6) 40 wt% SiO$_2$, 24.5 wt% CaO, 24.5 wt% Na$_2$O, 6 wt% P$_2$O$_5$, ZnO = 5 wt% SiO$_2$.

Fig. 5 — Infrared absorption spectra of bio-glasses:
(1) 45 wt% SiO$_2$, 24.5 wt% CaO, 24.5 wt% Na$_2$O, 6 wt% P$_2$O$_5$, and
(7) 43 wt% SiO$_2$, 12 wt% CaO, 23 wt% Na$_2$O, 6 wt% P$_2$O$_5$, 16 wt% CaF$_2$. 
Fig. 6 — Infrared absorption spectra of bio-glass No. 1
(45 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 0.6 wt% P₂O₅),
before and after immersion of different leaching solutions

Fig. 7 — Infrared absorption spectra of bio-glass No. 2
(40 wt% SiO₂, 24.5 wt% CaO, 24.5 wt% Na₂O, 0.6 wt% P₂O₅, B₂O₃ = 5 wt% SiO₂), before and after immersion of different leaching solutions
On immersing the base bioglass No. 1 in 1 M NaHCO₃ solution, the mid absorption bands are less intensified. The near-infrared broad band is more prominent and somewhat intensified and a new small absorption band is observed at ~1640 cm⁻¹. The far-infrared absorption band remains unchanged. A small kink is observed at about 1230 cm⁻¹.

On immersion of the base bioglass No. 1 in either simulated body fluid (S.B.F.) or tris solution, the absorption spectra become less intensified especially in the mid-absorption bands. Two small absorption bands can be identified at about 1460 and 1640 cm⁻¹. The far-infrared and near-infrared bands are unchanged. Also a small kink is observed at about 1230 cm⁻¹.
Fig. 7 shows the infrared absorption spectra of the bioglass No. 2, containing 5% B.O., before and after being immersed for 1 hr in the specified solutions. A comparison of the various absorption curves indicates that the overall spectra are characterized by highly resolved prominent bands especially in the mid-region and only minor changes are observed as can be summarized as follows:

(a) On immersion of the bioglass No. 2 in NaHCO₃ solution, the main absorption spectra remain nearly the same but with some minor changes. The absorption bands at about 710 cm⁻¹ and at about 1250 cm⁻¹ become less identified. A new sharp absorption is observed at ~1640 cm⁻¹ accompanied with the increase of the intensity of the near-infrared band at ~3650 cm⁻¹. In the far-infrared region, the band at ~300 cm⁻¹ in the base bioglass is absent in this bioglass containing 5% B.O..

(b) On immersing of the bioglass No. (2) in 0.1 M HCl solution, the mid absorption bands become less intensified. The absorption band at about 1485 cm⁻¹ is almost disappeared while the absorption band at about 750 cm⁻¹ shifts to longer wave-number at ~800 cm⁻¹. The absorption band at ~1640 cm⁻¹ is clearly resolved.

(c) On immersing of the bioglass No. (2) in either 0.1 M NaOH solution or 1 M Na₃PO₄ solution, the absorption spectra are almost identical keeping the characteristic bands as that obtained before immersion. The small kink at about 1380 cm⁻¹ is disappeared. With NaOH solution the small absorption band at ~1640 cm⁻¹ is disappeared.

(d) On immersing of the bioglass No. 2 in either simulated body fluid (SBF) or tris solution, the absorption spectra are nearly the same. The small absorption bands at ~1380 cm⁻¹ and the absorption band at 1640 cm⁻¹ is not resolved while the other bands remain as before immersion.

Fig. 8 reveals the infrared absorption spectra of the bioglass No. (3), containing 15% B.O., before and after being immersed for 1 hr in different specified leaching solutions. A careful look to the spectral curves indicates that the absorption spectra of bioglass No. 3 are somewhat similar to that of bioglass No. 2 consisting of several successive absorption bands in the mid-region extending from 450 cm⁻¹ to ~2000 cm⁻¹ but with moderate intensities. The observed changes of the spectra upon the immersion in the different leaching solutions can be summarized as follows:

(a) On immersion of the bioglass No. 3 in 0.1 M HCl solution, the intensities of all the mid-region absorption bands decrease and the far-infrared absorption spectra are clearly resolved.

(b) On immersion of the bioglass No. (3) in 0.1 M NaOH, 1 M NaHCO₃, or 1 M Na₃PO₄ solutions, the absorption spectra are nearly similar and showing the characteristic absorption bands of the base bioglasses but their peaks are rounded. The near-infrared broad band is prominent and the two absorption bands at 1485 and 1640 cm⁻¹ are clearly resolved. Also a kink at about 1230 cm⁻¹ is observed. In the same time, three successive small bands are observed at about 600, 750 and 820 cm⁻¹.

(c) On immersion of the bioglass No (3) in either simulated body fluid (SBF) or tris solution, the absorption spectra are very close and resembling the absorption spectra obtained after immersion in HCl solution. The intensities of the absorption bands in the mid-region are seen to decrease losing their sharpness.

Fig. 9 illustrates the infrared absorption spectra of the bioglass No. (4) containing 5 wt % Al₂O₃, before and after being immersed for 1 hr in various specified leaching solutions. A comparison of the spectral curves reveals the following:

(a) On immersion of the bioglass No. (4) in any of the solutions: NaOH (0.1 M), NaHCO₃, (1 M) or Na₃PO₄, (1 M), the absorption bands in the mid-region are intensified and the bands at about 450 and 1050 cm⁻¹ show very sharp and close peaks. However, the absorption bands at ~1485 and ~1640 cm⁻¹ are hardly identified. The near-infrared broad band at ~3650 cm⁻¹ and the far-infrared band at ~230 cm⁻¹ is unchanged while the other band at about 300 cm⁻¹ is hardly observed.

(b) On immersion of the bioglass No (4) in HCl solution (0.1 M) the overall absorption bands are well resolved but with less intensity than that obtained from the three Na-bearing solutions. The band at 1050 moves to about 1150 cm⁻¹ together with the resolution of a third peak at 1250-1300 cm⁻¹ and accompanied with the appearance of a moderate band at ~1640 cm⁻¹. A further small kink can be observed at ~600 cm⁻¹ and the band at about 480 cm⁻¹ moves to 460 cm⁻¹. The far-infrared spectrum is restricted to the resolution of one very sharp and
narrow band at 220 cm\(^{-1}\) while the near-infrared broad band is highly intensified.

Fig. 10 — Infrared absorption spectra of bio-glass No. 5 (40 wt% SiO\(_2\), 24.5 wt% CaO, 24.5 wt% Na\(_2\)O, 6 wt% P\(_2\)O\(_5\), MgO = 5 wt% SiO\(_2\)), before and after immersion of different leaching solutions

(c) On immersion of the bioglass No. (4) in either S.B.F or tris solution the absorption spectra in both cases are similar and identical to the spectra of the same bioglass before immersion.

Fig. 10 shows the infrared absorption spectra of the bioglass No. (5) containing 5% MgO before and after being immersed for 1 hr in various specified solutions. The spectral results can be summarized as follows:

(a) Inspection of the spectral curves due to the effects of sodium hydroxide, sodium bicarbonate and sodium phosphate reveals that the obtained spectra are similar and characterized by the sharp appearance of the mid-region absorption bands. Also it can be shown a strong band at about 1485 cm\(^{-1}\) and a kink or a curvature at about 1150 cm\(^{-1}\). In the far-infrared spectrum, a sharp absorption band is identified at about 220 cm\(^{-1}\) and a very small one around 280 cm\(^{-1}\). The near-infrared spectrum reveals a broad band centered at about 3650 cm\(^{-1}\). Also, a small band is observed at about 1230 cm\(^{-1}\).

(b) The spectral curve due to the effect of HCl solution reveals that the mid-region absorption bands are highly resolved and differ from that due to the effect of other solutions. The absorption band at 950-980 cm\(^{-1}\) sharply decreases in its intensity while the other absorption band at about 1150 cm\(^{-1}\) increases. A further prominent absorption band is resolved with a maximum at about 1300 cm\(^{-1}\). The absorption band at about 1640 cm\(^{-1}\) becomes prominent and the near-infrared broad absorption band near 3650 cm\(^{-1}\) is quite intensified. The absorption band at about 480 cm\(^{-1}\) is clearly identified accompanied with a curvature of a kink at about 600 cm\(^{-1}\). In the far-infrared absorption spectrum, a sharp band is observed at (220-230) cm\(^{-1}\) while the absorption band at (280-300) cm\(^{-1}\) is diminished.

(c) A comparison of the spectral curves showing the effects of both simulated body fluid (S.B.F) and tris buffer solution indicates that they give similar results to that of the un-immersed bioglass (5). This shows that these two solutions have eventually corrosion slight effects on this bioglass.

Fig. 11 reveals the infrared absorption spectra of the bioglass No. (6) containing 5% ZnO before and after being immersed for 1 hr in various specified solutions. The experimental results can be summarized as follows:

(a) Examination of the spectral curves obtained by immersing the bioglass 6 in various leaching solutions indicates that all solutions except HCl solution give the same spectra as that of the same
bioglass before immersion. This includes the general features, number and intensities of absorption bands in various regions of infrared spectrum. Exception is found only in HCl solution and NaOH solution where it is found that the second far-infrared absorption band at 280-300 cm⁻¹ diminishes whereas the first absorption band at 220-230 cm⁻¹ is intensified.

(b) On immersion of bioglass No. (6) in hydrochloric acid solution, noticeable changes are observed in some of the absorption bands position and intensity. The intensity of the absorption band at ~1050 cm⁻¹ increases and shifts to about 1100 cm⁻¹. A new absorption band is resolved at about 1250 cm⁻¹. A further absorption band is resolved at ~1640 cm⁻¹. The broad near-infrared absorption centered at 3650 cm⁻¹ is intensified. Also, the absorption band at 480 cm⁻¹ is clearly resolved and a secondary neighbouring peak or inflection is observed at ~600 cm⁻¹.

Fig. 12 shows the infrared absorption spectra of the bioglass No. (7) containing 16% CaF₂ before and after being immersed in specified leaching solutions for 1 hr. The spectral curves variations can be described as follows:

(a) Inspection of the spectral curves indicates that the immersion in any of the solutions of sodium hydroxide, sodium bicarbonate, sodium phosphate or hydrochloric acid leads to fair resolution of all the absorption bands extending in various regions of the infrared spectrum.

(b) On immersion of the bioglass No. (7) in S.B.F. or tris buffers, the absorption spectra obtained are the same observed of the bioglass No. (7) before immersion and they are generally weak enough to be hardly identified.

4. Discussion

4.1 Theoretical considerations

Over the last several decades, many investigators have found that the analysis of vibrational spectra of glasses can be applied to the solution of both the industrial and basic research problems. In an applied study, the vibrational spectra can be used to identify the specific groups which are present in glasses. However, in a theoretical study, information can be obtained concerning the fundamental structural nature of glasses in which their properties are dependent.

The lack of long-range order in glasses prevents the use of X-ray diffraction in studying their structure. Techniques have been developed in which one determines the radial distribution functions of electron densities about specific atoms. The results of this type of investigation are limited because the symmetry and extent of short range ordering cannot be adequately resolved. Analysis of the vibrational
spectra, however, can provide structural information when a thorough theoretical analysis of the data is carried out. In addition, vibrational spectra can be readily used to identify the presence of defect groups within a glass. Infrared spectroscopy has also been used to identify low-concentration impurities such as water, hydroxyl ions, etc. in glass.

4.2 Infrared spectroscopy and glass structure

Infrared spectroscopy is a powerful analytical technique which provides molecular level information on functional groups of both inorganic and organic materials. Sample preparation is minimal, the measurement is non-destructive and small amounts of material (micrograms to nanograms) can be analyzed.

Infrared spectroscopy has been recently used to study the aqueous corrosion of glass. This is typically performed using thin slices of glass, having thickness of approximately (0.5-1) mm. With such samples, infrared transmission spectroscopy is effective down to about 2000 cm⁻¹. As a result, studies of this type tend to focus on the main water bands in the 3800-2500 cm⁻¹ range, but miss the structural vibrations of the glass-forming network in the 1200-200 cm⁻¹ range.

Hench et al. have shown how infrared reflection spectroscopy (IRR) can be used to follow the effect of water on the structural bands of glass. Also this tool is currently utilized to study the surface reactions of bioactive glasses upon the immersion in leaching solutions such as simulated body fluid.

The KBr pellet technique for infrared spectroscopy has been much recently used to study the structure of different types of glasses including silicates and borates in the range 4000-200 cm⁻¹ (Refs 11-15). The information obtained from these studies are found to be fruitful in elucidating the network structure arrangements in such glasses.

4.3 Interpretation of infrared results

To explain and understand the results obtained from infrared absorption measurements the following criteria must be taken into consideration:

(1) Glass is considered as non-crystalline solid which lacks periodicity in its internal structure arrangement. This makes the elucidation of its structure very difficult even by X-ray diffraction analysis.

(2) Infrared absorption measurements of various types of glasses give absorption bands which are finger-print to confirm the presence of building units in comparison of the same units in the crystalline solids.

(3) The chemical composition of the basic
Table 1 — Chemical composition of bioglasses studied (Wt. %)

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Table 2 — Assignment of the infrared absorption bands present in the spectra of the base bioglass

Peak position (cm⁻¹) | Assignment                                                                 | References |
---------------------|---------------------------------------------------------------------------|------------|
(1) Network former   |                                                                           |            |
(a) Silicate chains  | Si-O-Si anti-symmetric stretching of bridging oxygens within the tetrahedra (v₄) | 21 & 22    |
1065-1095            |                                                                           |            |
940-970, 1010        | Si-O stretching (with 1 non-bridging oxygen)                              | 21 & 22    |
866-928              | Si-O stretching (with 2 non-bridging oxygens)                            | 21 & 22    |
746-818              | Si-O-Si symmetric stretching of bridging oxygens between tetrahedra       | 21 & 22    |
460-506, 600         |                                                                           |            |
(b) Phosphate chains | Si-O-Si and O-Si-O bending modes (v₄)                                    | 21 & 22    |
1200-1320            | (PO₄)³⁻ asymmetric stretching                                            | 28 & 30    |
1270-1290            | P=O                                                                       | 28 & 30    |
1020-1200            | (PO₄)³⁻ terminal group symmetrical stretching                             | 28 & 30    |
900-1090             | (PO₄)²⁻                                                                  | 28 & 30    |
940-950              | (PO₄)¹⁻                                                                  |            |
850-1050             | P-O-P asymmetric stretching                                              |            |
600-800              | P-O-P symmetric stretching                                               |            |
560-668              | P-O-P bending                                                             |            |
(2) Network modifiers|                                                                           |            |
280-350              | Na-vibration frequency                                                    | 22, 25, 30 & 31 |
200-250              | Ca-vibration frequency                                                    | 22, 25, 30 & 31 |
1450, 230            | Carbonate group                                                           | 16, 21, 22, 30 & 31 |
866-960              | C-O stretching (v₃)                                                       | 16, 21, 22, 30 & 31 |
3600-3750            | SOH (Silanol group)                                                       | 16, 21, 22, 30 & 31 |
3200-3500            | Molecular water                                                           | 16, 21, 22, 30 & 31 |
2700-3000            | Hydrogen bonding                                                          | 16, 21, 22, 30 & 31 |
1640                 | Molecular water                                                           | 16, 21, 22, 30 & 31 |

Bioglass consists of the same basic constituents to be found in the industrial sheet and tableware glasses together with some small variation. Basic bioglass contains SiO₂ 45%, Na₂O 24.5%, CaO 24.5%, P₂O₅ 6% as the chemical constituents.
(4) It is expected, therefore, that certain specified building groups are present in the internal structure of the bioglass including silicate groups [ SiO₄ ] and either single or polymer chain network and also phosphate groups [ PO₄ ]. Such network-building groups give usually characteristic absorption bands in the mid-region of the infrared spectrum (400-2000) cm⁻¹.

(5) The infrared spectrum also includes absorption bands which eventually originate from vibrations of network modifiers such as Na or Ca and these absorption bands are extending in the range of far-infrared (100-400) cm⁻¹.

(6) The infrared spectrum also includes absorption bands belonging to the near-infrared region (2000-4000 cm⁻¹) which includes absorption bands due to hydroxyl group, water band or Si-OH silanol group.

It should be realized, however, that the assignments employed in this work given in Tables 2-3 are based on the vibrational spectra of characteristic crystalline compounds of known structure beside that deduced from related cited publications.

4.3.1 Interpretation of infrared results obtained before immersion

The infrared results obtained before immersion can be explained as follows:

(1) The base bioglass of the composition SiO₂ 45 %, Na₂O 24.5, CaO 24.5, P₂O₅ 6% before immersion shows seven absorption bands in the middle region, two absorption bands in the far-infrared region and one broad absorption band in the near-infrared region. The previous absorption bands can be attributed to the following specific groups or cations vibrations:

(A) Mid-region (characterized by network forming units)

(a) Strong absorption band at 500-480 cm⁻¹ which can be attributed to Si-O-Si or O-Si-O bending modes.

(b) Very weak inflection or kink at about 600

Table 3 — Assignment of other infrared absorption bands

<table>
<thead>
<tr>
<th>Peak position (cm⁻¹)</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>B-O bonds</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1250</td>
<td>B-O vibration of various borate rings</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1250-1270</td>
<td>Boroxol rings, tri-tetra- and pentaborate groups</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1350-1400</td>
<td>Pyro- and ortho units</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1420-1550</td>
<td>Tri-, tetra-, and pentaborate groups</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1520</td>
<td>Diborate groups</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1600-1700</td>
<td>Oxygen bridges between two trigonal groups</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1750-1850</td>
<td>Oxygen bridges between two trigonal aroms</td>
<td>15, 21, 23, 27 &amp; 32</td>
</tr>
<tr>
<td>1950-2050</td>
<td>Al₂O₃ groups</td>
<td>15 &amp; 27</td>
</tr>
<tr>
<td>396-406</td>
<td>MgO groups</td>
<td>27</td>
</tr>
<tr>
<td>485</td>
<td>ZnO groups</td>
<td>27</td>
</tr>
</tbody>
</table>
cm⁻¹ which can be also correlated to the previous bending vibration.

(c) Very weak inflection at 800-700 cm⁻¹ which can be assigned to Si-O-Si symmetric stretching of bridging oxygens between tetrahedra.

(d) Strong absorption band at 950-980 cm⁻¹ which can be related to Si-O- stretching with one or two non-bridging oxygens.

(e) Very strong absorption band at 1120-1050 cm⁻¹ which can be assigned to Si-O-Si antisymmetric stretching of bridging oxygens within the tetrahedra.

(f) Very weak inflection at 1430-1490 cm⁻¹ which can be related to carbonate group.

(g) Very weak inflection at 1630-1670 cm⁻¹ which can be attributed to the molecular water

(B) Near-infrared region (characteristic for water, hydroxyl and silanol groups)

(h) Very strong broad band centered at 3500-3600 cm⁻¹ which can be assigned to hydroxyl group (OH) or silanol group (Si-OH).

(C) Far-infrared region (characteristic cation-oxygen bonding vibration)

(i) Very sharp narrow band at 280-300 cm⁻¹ which can be related to Na-vibration frequency.

(j) Sharp narrow band at about 220 cm⁻¹ which can be attributed to Ca-vibration frequency.

The above absorption spectra obtained from the base bioglass are nearly the same obtained by various authors from the traditional soda-lime-silica glasses. The introduction of 6% P₂O₅ in the bioglass composition has small significant difference between the absorption spectrum of both the bioglass from that of ordinary soda lime silica glass. This is eventually due to the fact that most of the positions of the characteristic absorption spectra due to phosphate chains are very close to the positions of the silicate chains. The above frequencies of phosphate chains are not separately resolved due to the interference of the silicate chains which are present in major proportion (45 wt %) while the P₂O₅ content is minor (6 wt %).

1. Effect of boric oxide (B₂O₃) Fig. 11 shows the infrared absorption spectra of the bioglass No. (2) containing 5 wt% B₂O₃ and bioglass No. (3) containing 15% wt% B₂O₃, together with the base bioglass No. (1). The spectral curves of the bioglasses No. (2) and No. (3) reveal several additional absorption bands in the mid-region which can be related to various borate groups. Some of the borate groups especially that due to B₂O₃ tetrahedra give absorption bands which coincide or interfere with the absorption bands due to the silicate groups. The net result is that the absorption bands extending from 700 to about 1200 cm⁻¹ are really composite ones of the two silicate chains and borate phases (mainly B₂O₃) groups. The absorption bands which are observed at (1250-1500) cm⁻¹ are mainly due to BO₃ stretching (these assignments can be followed in Table 2. However, bioglass No. (3) containing 15 wt % B₂O₃ reveals lower intensity of the composite bands extending from 450 to 1150 cm⁻¹ and this can be correlated with the cessation of B₂O₃ formation and the abundance of BO₃ groups. This can be confirmed by the sharp decrease of the absorption band at 280-330 cm⁻¹ in the bioglass No (2) containing 5 wt % B₂O₃ and the reappearance with moderate intensity in the bioglass No. (3) containing 15 wt % B₂O₃. This is due to the tightening effect of Na cations in the vicinity of BO₃ groups to neutralise the excess negative charge from the surplus oxygen in the four coordination process of the boron ions. Another postulation is that the decrease in the intensity of the composite band 450-1150 cm⁻¹ can be correlated with the decrease of the silica content to 30 wt %.

The previous assumptions regarding the vibrational frequencies of borate chains can be supported by the work of Krogh-Moe⁶ and Kamitsos et al⁶. These authors have shown that the vibrational modes of the borate network are mainly active in three infrared spectral regions:

1. 1500-1200 cm⁻¹ (B-O stretching of trigonal B₂O₃ units),
2. 1200-850 cm⁻¹ (B-O stretching of tetrahedral B₂O₃ units), and
3. 800-600 cm⁻¹ (bending vibrations of various borate species).

It is obvious that the frequencies of the borate chains are very close and interfere with the frequencies of the silicate chains. It is thus expected that silicate glasses containing varying amounts of B₂O₃ should contain composite vibrational modes due to the combined presence of both silicate and
Formation of borate chains with varying degrees.

The different vibrational behaviour observed with bioglasses No. (2) and (3) containing 5 wt. % and 15 wt. % B.O., can be correlated with the change of the boron-coordination with glass composition. Kamitsos et al., have shown that the absorption spectra of borate glasses give indication of the initial creation of BO₄ tetrahedra and after a certain limit it is observed the subsequent cessation or destruction of the BO₄ groups in favour of the formation of non-bridging oxygen-bearing units. This explains that in bioglass No. (3) containing 15 wt. % B.O., the absorption bands due to BO₄ groups would relatively decrease and replaced by the formation of non-bridging oxygens.

(2) Effect of aluminium oxide (Al₂O₃) Fig. 2 reveals the absorption spectrum of the bioglass No. (4) containing 5 wt. % Al₂O₃ together with the base bioglass No. (1). The absorption spectrum of Al₂O₃-containing bioglass No. (4) shows prominent mid absorption bands with rounded peaks. The intensity and width of the bands increase for the absorption bands at 440-500 cm⁻¹. This may be attributed to the formation of some Al₂O₃ groups which are known to give absorption band at 396-496 cm⁻¹ (Ref. 15). Thus the observed absorption band at 440-580 cm⁻¹ is a composite one originating from the bending vibrations of Si-O-Si or O-Si-O modes together with that due to the vibrations of [Al₂O₃] groups coinciding and overlapping each other. A support of this assumption is that the far-infrared absorption band due to Na cation vibration at 280-300 cm⁻¹ sharply decreases. This indicates that Na⁺ cations are tightened to the (Al₂O₃) groups to keep electrical neutrality and, therefore, are not able to vibrate freely.

Also Fig. 2 shows the pronounced increase and shifting to lower wavenumbers of the two absorption bands at about 920 and 1020 cm⁻¹. This may be rationalized by assuming that some Al⁺ cations substitute Si⁺ cations and the formed SiO₃-Al groups give absorption bands having vibrations of lower wavenumber. This new structural groupings containing alumina are generally stronger and giving better chemical stability and, therefore, the near-infrared absorption band due to water and OH-groups at about 3650 cm⁻¹ is decreased. The far-infrared absorption band at ~230 cm⁻¹ due to Ca⁺ cations vibrations are free to vibrate in such bioglass structure. The previous assumptions are confirmed by the work of Merzbacher and White. They suggested that aluminium acts as a network-former in some silicates replacing Si in tetrahedral coordination. The net-negative charge due to this substitution is neutralized by a nearby network-modifier. They also added that the strong infrared absorption band between 700 and 900 cm⁻¹ due to condensed Al₂O₃ framework units could be assigned to the 908 cm⁻¹ mode.

(3) Effect of magnesium oxide (MgO) Fig. 3 shows the infrared absorption spectrum of the bioglass No. (5) containing 5 wt. % MgO together with the spectrum of base bioglass No. (1). The spectrum reveals highly resolved prominent absorption bands especially in the mid-region. Seven absorption bands are observed in the mid-range from 400-1700 cm⁻¹. The strong absorption bands at about 480, 920 and 1060 are shifted to shorter wavenumbers to reach about 440, 880 and 980 cm⁻¹ accompanied by marked intensity. This can be realized and interpreted by assuming that Mg⁺ can occur in tetrahedral coordination giving strength to the structure. If Mg⁺ is acting in part as a network-former, then the silicate structure would be more polymerized and the more polymerized stretching frequencies occur at shorter wavenumbers. If magnesium is acting as a network-former in tetrahedral coordination, then the charge balance must be maintained by alkali cation. Merzbacher and White assumed that magnesium can form MgO in silicate glasses and it seems that the spectra of such group are buried in the low-frequency shoulder of the mid-frequency network-bending mode of silicate chains. Experimental results indicate that the strong observed absorption band at ~440 cm⁻¹ with its lobe at 480 cm⁻¹ is a composite one consisting of both bending mode of Si-O-Si and MgO bands together. This is also confirmed by Nelson and Exarhos who observed a MgO vibrational mode at 325-400 cm⁻¹. The diminishing or absence of the far-infrared absorption band due to Na⁺ cations at 280-300 cm⁻¹ because of the thickening of Na cations to MgO, for electrical neutrality supports the previous assumption.

(4) Effect of zinc oxide (ZnO) Fig. 4 reveals the absorption spectrum of the bioglass No. (6) containing 5 wo % ZnO together with that of the base bioglass No. (1). The spectrum shows highly
resolved mid-absorption bands in the range 400-1700 cm\(^{-1}\). The absorption bands at about 480, 920 and 1060 in the base bioglass are shifted in this glass to shorter wavenumbers to reach to 440, 880 and 980 cm\(^{-1}\) accompanied by marked intensities. Such behaviour may indicate stronger and coherence of the network structure. This can be realized by assuming that \(\text{Zn}^{2+}\) cations can occur in tetrahedral coordination. Khedr and El-Batal\(^{10}\) have supported the view that \(\text{Zn}^{2+}\) can form \(\text{ZnO}\) group. In this situation, the presence of further extra network-forming units lead to polymerization of the silicate structure and the more polymerized stretching frequencies occur at shorter wavenumbers. If zinc cation is acting as a network-former in tetrahedral coordination, then charge balance would be satisfied by alkali cations. Dean\(^{11}\) has suggested that \(\text{ZnO}\) groups can give absorption frequency at 400-500 cm\(^{-1}\). The absorption spectra of such groups are formed very close and interfere with the bending vibration of Si-O-Si linkages and both vibrations reveal a composite broad and sharp band centered at about 440 cm\(^{-1}\) and the appearance of a tail at about 480 cm\(^{-1}\). The silicate chains are obviously greatly resolved and intensified and are exemplified by the strong appearance of the absorption bands at about 750, 920, 1030 and 1470 cm\(^{-1}\) beside the presence of a kink at about 600 cm\(^{-1}\). The combined presence of all these absorption bands supports the view that more polymerized chains might be present in the structure of this bioglass.

(5) Effect of calcium fluoride (CaF\(_2\)) Fig. 5 shows the absorption spectrum of the bioglass No. (7) containing 16 wt.% CaF\(_2\); together with that of the base bioglass No. (1). The spectrum reveals one small absorption band in the mid region at about 1100 cm\(^{-1}\) and three hardly-identified bands at about 500, 1480 and 1640 cm\(^{-1}\) and a small near-infrared broad band at about 3550 cm\(^{-1}\). Also at the far-infrared region, two very small kinks at about 230 and 350 cm\(^{-1}\) can be identified.

The experimental results can be correlated with the role of CaF\(_2\) in the glass structure. It is known that calcium fluoride is frequently used in the production of opacified glasses and controlled crystalline glass-ceramics. The effect of calcium fluoride can be understood by recalling that the fluorine ion, with a radius of 1.36 \(\text{Å}\), is very close in size to the oxygen ion (radius 1.40 Å) so that a fluorine ion would replace an oxygen ion in the glass network without causing too great disturbance in the arrangement of other ions\(^{8}\). Since the fluorine ion is monovalent, however, the over all replacement within the glass must be of two fluorine ions for each oxygen ion in order to ensure electroneutrality. A general effect of the introduction of fluorine would be to replace strong Si-O-Si linkages by pairs of Si-F\(^{-}\) linkages with the result that the glass network structure would be weakened.

It seems that the introduction of such high percentage of CaF\(_2\) (\(\sim\)16 wt. %) causes a large number of nuclei to be distributed all over the glass causing the weakening of the network and the decrease of the intensity of the absorption peaks. However, when this prepared bioglass containing CaF\(_2\) is immersed in solutions, the dispersed numerous nuclei are assumed to be dissolved and the absorption spectra of the bioglass restores the characteristic absorption bands.

4.3.2 Interpretation of infrared absorption after immersion

Inspection of the experimental results Figs 6 to 12 comprising the absorption curves of selected studied bioglasses obtained after immersion in specified solutions indicate that the infrared spectra depend on the chemical composition of the bioglass and the type of leaching solution. The results can be understood and interpreted as follows:

(1) Base bioglass after immersion

(a) The slight effect of all immersing solutions on the base bioglass except that of NaOH and NaPO\(_3\) solutions, indicate that this basic bioglass is stable towards the action of almost all different solutions.

(b) The marked decrease of the intensity of the absorption band at 920-940 cm\(^{-1}\) which is related to Si-O- with 1 or 2 non-bridging oxygens can be correlated with the ion-exchange process between hydrogen or hydronium ions from aqueous solutions and the sodium ions from the surface of the bioglass according to the following reaction:

\[
\text{Si-ONa + H}_2\text{O} = \text{Si-OH} + \text{NaOH}
\]

(c) The confirmation of this ion exchange process is visualized by the obvious increase of the near-infrared absorption broad band at 3550 cm\(^{-1}\) together with the appearance of the absorption band at about 1640 cm\(^{-1}\). These two absorption bands are
assigned to Si-OH groups and molecular water, respectively.

(d) The formation of Si-OH will eventually leads to surface silica gel layer.

(e) The observation of a small kink at 1230-1270 cm\(^{-1}\) can be correlated with phosphate chain (either P-O or PO\(_4\)) asymmetric stretching.

(f) Sodium hydroxide and sodium phosphate solutions are shown to decrease the overall spectra. This behaviour can be rationalized by assuming that the action of these two specific solutions is different than the action of the other immersion solutions. These two solutions can corrode both silica and alkali at the same time, i.e., total dissolution is expected in this case. This explains their corrosive action on the base bioglass.

(2) Effect of boric oxide The experimental infrared absorption spectra obtained after immersion of bioglasses (2) and (3) are shown in Figs 7 and 8 and can be explained as follows:

(a) The spectra obtained after immersion of bioglass No. 2 containing 5 wt. % B,O\(_3\) in all solutions except HCl solution indicate the persistence of the highly resolved and intense mid absorption bands with the same features as the same bioglass before immersion but with some changes. In HCl solution, the mid absorption bands sharply decrease in their intensities. This behaviour can be related to the high solubility of the borate phase in acidic HCl solution and thus reduces some of their characteristic absorption bands while the bands of the silicate phase remain unchanged. This conclusion may support the assumption that in borosilicate glasses, two phases may exist as separate borate and silicate ones or even present as microphase separated phases.

(b) The absence of the far-infrared absorption band at about 260-330 cm\(^{-1}\) which is assigned to Na\(^+\) cation vibration can be explained by assuming that some of the introduced B,O\(_3\) form tetrahedral BO\(_3\) groups by accepting a fourth oxygen which is electrically neutralized by a firmly attached Na\(^+\). Thus the attached Na\(^+\) cations are not free to vibrate easily as when situated in interstitial positions between silicate chains.

(c) In immersing the bioglass No. (2) in the leaching solutions, it is expected that some of the Na\(^+\) ions in the surface of the glass are replaced by hydrogen or hydronium ions from the solutions and Si-OH silanol groups are formed. The confirmation for the formation of such Si-OH groups is realized by the formation of the absorption band at ~1650 cm\(^{-1}\) due to molecular water and the intensification of the broad near-infrared absorption band centered at about 3550 cm\(^{-1}\) due to silanol groups.

(d) The mid absorption band at 920-980 cm\(^{-1}\) is not decreased or disappeared on the immersion of bioglass No. (2) in leaching solutions as observed in the base bioglass No. (1). This can be explained by assuming that in the former bioglass, the observed spectrum consists of combined vibrations of both non-bridging silicate stretching and BO\(_3\) stretching modes. The immersion in the leaching solutions is assumed to change the position or entity of the non-bridging silicate vibration only but the second BO\(_3\) stretching remains in the same position.

(e) The absorption spectrum of bioglass No. (3) containing 15 wt. % B,O\(_3\) is less intensive than the absorption spectrum of bioglass No. (2) containing 5 wt. % B,O\(_3\). This can be understood by assuming that the spectrum of bioglass No. 3 consists mainly of vibrations of silicate chains (30% SiO\(_2\)) and BO\(_3\) groups and the sharing of BO\(_3\) groups vibrations is low. On the other band, the spectrum of bioglass No. (2) consists of collective vibrations of silicate chains (40% SiO\(_2\)), BO\(_3\), and BO\(_3\) groups.

A confirmation of this hypothesis can be followed by the reappearance of the far-infrared absorption band at 280-350 cm\(^{-1}\) which indicates that some of the Na\(^+\) cations are free to vibrate in their cited position in the bioglass No. (3) containing 15 wt. % B,O\(_3\). Also the absorption band at about 1480 cm\(^{-1}\) is observed to be strong due to the presence of relatively more BO\(_3\) groups. A further support is visualized by the decrease of the intensity of the absorption band at 920-950 cm\(^{-1}\) and the formation of silanol SiOH groups and giving rise to the simultaneous appearance of the absorption band at about 1640 cm\(^{-1}\). Also it is observed that hydrochloric acid solution leaches the borate phase in bioglass No. 3 as it does in bioglass No. (2) and the net result is that the observed absorption spectra are mainly related to silicate chains.

(3) Effect of aluminium oxide (Al₂O₃) The infrared absorption spectra of the bioglass No. (4) containing 5 wt. % Al₂O₃ before and after immersion in different selected solutions are shown in Fig. 9.
and the results are understood and explained as follows:

(1) Inspection of the spectrum of the bioglass No. (4) before immersion reveals the same characteristic absorption bands as the base bioglass No. (1). This can be understood by assuming that Al\(^{3+}\) ions can be isomorphously introduced in the silicate structure to substitute Si\(^{4+}\) ions by accepting a surplus oxygen to form [AlO\(_4\)] groups and the excess negative charge is balanced by a nearby firmly attached Na\(^+\) cation. Merzbacher and White\(^2\) assumed that the isomorphous substitution of Al\(^{3+}\) for Si\(^{4+}\) is accompanied by the shift of the mid-absorption bands to longer wavenumber. This assumption is supported by the observation of the marked decrease of the far-infrared absorption at about 280-330 cm\(^{-1}\) which is assigned to the vibrations of Na\(^+\) cations. The Na\(^+\) cations which are assumed to be firmly attached to (AlO\(_4\)) groups are not free to vibrate as in the case of being housed in interstitial positions within the silicate chains.

(2) On checking the effect of solutions of sodium hydroxide, sodium bicarbonate and sodium phosphate, the absorption spectra reveal highly resolved intensified mid-absorption bands at about 480, 750, 1010 and 1030 cm\(^{-1}\). The mentioned three solutions are highly alkaline and they are expected to corrode heavily traditional soda-lime-silica glass. However, the bioglass No. (3) containing 5% AlO\(_2\) reveals spectral evidence indicating the prevalence of stronger silicate chains. This can be explained by assuming that the attacking solutions comprising NaOH by itself or by hydrolysis would produce thin layer of gelatinous Al(OH)\(_3\) precipitate on the surface of the bioglass No. (3) prohibiting further attack. Also, it is expected that the primarily formed silanol Si-OH groups would perform auto-reaction of the type:

\[
[Si-OH + HO-Si] = [Si-O-Si]H_2O
\]

This gives strength to the silicate chains.

(3) The effect of hydrochloric acid solution is quite different and reveals the pronounced decrease of the 920 cm\(^{-1}\) band intensity indicating the transformation of some non-bridging oxygens to form silanol Si-OH groups which are observed to give marked stretching vibrations at about 1640 cm\(^{-1}\) and about 3650 cm\(^{-1}\). Also with HCl solution a new small absorption band can be observed at 1230-1270 cm\(^{-1}\) which can be ascribed to the phosphate groups vibrations. It thus evident that on the immersion in HCl solution the presence of silanol groups leading to the surface silica gel layer together with the formation of another layer rich in P-O, which several workers Kokubo\(^1\), Hench\(^1\) have identified as a hydroxyapatite surface layer being responsible for the bonding of bioglass with bone.

(4) The spectral curves in Fig. 9 show the effects of SBF or tris buffer solution which indicate no visual changes and assuming that the bioglass No. (4) containing 5 wt. % AlO\(_2\) is quite stable towards the action of these two specific solutions.

(4) Effect of magnesium oxide (MgO) The infrared absorption spectra of the bioglass No. (5) containing 5 wt. % MgO before and after immersion in different selected solutions for 1 hr at 95°C are shown in Fig. 10 and the results can be interpreted as follows:

(1) All the absorption spectra obtained after immersion in various solutions except HCl solution are comparable and having nearly the same effect comprising the specific absorption bands characteristic for silicate, phosphate chains and MgO, groups beside network modifiers vibration and that due to water and hydroxyl groups.

(2) In all the absorption spectra obtained, the far-infrared absorption band at about 280-350 cm\(^{-1}\) is diminished and this can be related to the close attachment of the Na\(^+\) cations to the already formed [MgO\(_4\)] to compensate for the surplus negative charge. Therefore, such attached Na\(^+\) cations are not free to vibrate.

(3) The immersion of bioglass No. (5) in hydrochloric acid solution (0.1 M HCl) gives different effect in which the absorption spectrum which indicates that the corrosion proceeds by ion-exchange process involving the substitution of Na\(^+\) at the terminal of the non-bridging oxygen with hydrogen (or hydronium) ion from HCl solution leading to the formation of silanol (Si-OH) groups. This formed silanol groups vibrate at the frequency position of 3650 cm\(^{-1}\) and is accompanied by the absorption band at 1640 cm\(^{-1}\) due to molecular water. This is also accompanied by the decrease of the absorption band at 920 cm\(^{-1}\) intensity.

(4) The spectral curves in Fig. 10 show the
effect of S.B.F and tris buffer solution on the absorption spectra of bioglass No. (5) which indicate similar trend assuming that the bioglass is stable towards the action of these solutions.

(5) Effect of zinc oxide (ZnO) The infrared absorption spectra of the bioglass No. 6 containing 5 wt.% ZnO before and after immersion in different solutions for 1 hr at 95°C are shown in Fig. 11 and the results obtained can be explained as follows:

(1) All the investigated immersion solutions except HCl give approximately similar effect revealing characteristic absorption bands due to silicate and phosphate chains and most of them are close and coincide together but with the abundance of silicate as a major constituent (~45 wt.%).

(2) The detailed effect with ZnO are the same as obtained with MgO and can be discussed on the same basis by assuming the ability of ZnO to form ZnO$_2$ groups.

Effect of calcium fluoride (CaF$_2$) The infrared absorption spectra of the bioglass No. (7) containing 16 wt.% CaF$_2$ before and after immersion in different leaching solutions for 1 hr at 95°C are shown in Fig. 12 and the results can be explained as follows:

(1) The effect of hydrochloric acid, sodium hydroxide, sodium bicarbonate and sodium phosphate on this bioglass are found to be similar. This indicates the resolution of the characteristic absorption bands usually observed in base bioglass No. (1) comprising that due mainly to silicate chains and some phosphate groups together with far-infrared absorption related to Na$^+$ and Ca$^{2+}$ cations vibrations and also to water, hydroxy and silanol bands. The difference between the various solutions can be explained by assuming that these solutions are either acidic or alkaline in nature. In acidic solution, the corrosion mechanism proceeds by ion exchange while in alkaline solution the corrosion is bulk dissolution.

(2) The effects of both S.B.F and tris solutions are found to be negligible due possibly to their buffering action.

References
