Characterization of bioactivity in transition metal doped-borosilicate glasses by infrared reflection and dielectric studies

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Borosilicate glasses with the addition of one of the 3d-transition metals (Ti/Cu) (0.1 g/100g glass) have been investigated as possible materials having bioactivity by infrared reflection spectroscopy and electrical properties after the immersion in simulated body fluid (SPF) for different interval of times. The results show obvious effects of the transition metal ions on the bioactivity of the borosilicate glasses. The results are discussed taking into consideration recent achievements that govern the formation of hydroxyapatite surface layer on glass. Also, IR and electrical results are discussed in relation to the glass composition and structure, which confirm the effect of the formation of HAp layer and the possible mixed ionic and electronic mechanisms due to the addition of transition metal oxides.

Keywords: Bioactivity, Borosilicate glass, Transition metals, Infrared reflection, Dielectric property

I Introduction

Borosilicate glasses are of technological interest because they have many and diverse applications. They generally have lower thermal expansion values, good chemical resistance, high dielectric strength and higher softening temperatures than other commercial glasses. For these reasons they are used for many applications such as glassware, industrial piping, bulbs for hot lamps and also they are recently investigated as for immobilization of nuclear wastes, possible materials that could perform bioactivity.1,2

The mechanism of bonding of bioactive glasses with living tissues has been reported to be associated with the development of a layer consisting of carbonate-containing hydroxyapatite (HCAp) similar to that of bone on the surface of the materials.3-5 Series of reactions with their kinetics that take place on the surfaces of these glasses after immersion in tissues or experimental fluids, are responsible for the onset of the apatite formation.6-8 The reaction stages begin with ion exchange of alkali and alkaline earth ions such as Na+, K+ and Ca2+, from the glass with H3O+ or (H)+ from the body fluids or simulated physiological solutions and subsequent network dissolution through progressive attack of the silica structure by hydroxyl ions.9 Hydroxyapatite (HAp) belongs to the hexagonal system with a space group P63/m and is characterized by a six-fold c-axis perpendicular to three equivalent a-axes at angles of 120° to each other. The dimensions of the unit cell of HA are a-axis=0.9422nm, c-axis=0.6880nm. This produces a layer of silanols (Si-OH) on the glass surface through which [Ca]2+ and [PO4]3- ions migrate from surrounding fluids and form an amorphous CaO-P2O5. rich film, which finally crystallizes to HCAp by incorporation of OH and [CO3]2- from the surrounding tissues.

The mechanism for the nucleation and growth of these calcium-based phases on bioglass is still not completely clear, but a number of hypotheses have been proposed in many publications.3,8 Meanwhile, work by Li and colleagues11 concluded that the combination of a large number of hydroxyl groups and negative charges on the bioactive gel surface are necessary for the induction of HCAp. They demonstrated that the negative charge would accumulate cations such as Ca2+ on the surface and would ultimately lead to precipitation of calcium phosphate. In other publications12 on bioactive glasses, it has been shown that the high surface area provides a high concentration of surface silanol groups (Si-OH) that serve as nucleation sites for the crystallization of HCAp. Karlsson et. al13 have proposed that the silanol groups on the gel layer are
flexible enough to supply the correct atomic distances required by the crystal structure of HCAp.

The most commonly reported simulated physiological solution used for testing the potential behaviour of bioactive glasses is Simulated Body Fluid (SBF) described by Kokubo et al. This solution contains ion concentrations such as Na+, K+, Ca2+ or Mg2+ and has pH and temperature similar to those of human blood plasma and it has been reported that it is capable of forming HCAp with small crystallites and defective structure on the surface of bioactive on the surface of bioactive ceramics.

Bioactive glass powder, 45S5 Bioglass®, a commercially available Bioglass® Synthetic Bone Graft Particulate has been successfully used as an allograft for treatment of osseous defects and bone loss in periodontal disease. In the last decade, many electrical and optical studies on binary glass systems based on borate glasses containing different transition metal oxides have been reported. Now-a-days these glass systems are important in the field of laser and infrared detection technique. In general, it is somewhat difficult in these glass networks to identify the conduction mechanisms whether it is ionic or electronic especially if the concentrations of transition metal oxides are varying to large extent. Recently several attempts have been made to explain the possible conduction mechanisms in the binary glass systems.

The aim of this study is to investigate the development of HCAp layer on the surface of an undoped bioactive borosilicate glass and other derivatives glasses of the same basic composition but containing 0.1% of one of the first row transition metals (Ti↔Cu) in the form of its oxide after immersion in SBF-K9 solution using FTIR reflectance spectroscopy and also measuring their dielectric properties to justify the progressive formation of HCAp layer after 2 weeks of immersion in SBF.

### 2 Materials and Methods

#### 2.1 Preparation of glass

The base borosilicate glass of the chemical composition SiO2 74%, Na2O 16%, B2O3 10% (mol%) and their derived 8 batches were weighed and each containing 0.1/100g glass from one of the oxides of the transtransition metal ions (Ti↔Cu). The glasses were prepared by melting chemically pure raw materials. Quartz was used as the source of silica; soda was added in the form of its respective anhydrous carbonate, and orthoboric acid (H3BO3) was introduced as a source for boric oxide. Melting was conducted in a platinum crucible in an electrically heated furnace at 1450°C +20°C. Melting was continued for 2 h after the addition of the batch and the melt was rotated at intervals to promote complete mixing and homogeneity. The melts were cast in preheated rectangular stainless steel molds of the dimensions 1x1x4 cm3. The prepared glass samples were transferred immediately to be annealed in a muffle furnace regulated at 450°C. The muffle after 1 h was then switched off to cool to room temperature at rate of 30°C/ h.

#### 2.2 Surface analysis of borosilicate glasses using infrared reflection spectroscopy

In order to investigate the possible formation of the calcium phosphate layer formed on the surface of the glass samples after immersion in simulated body fluid (SBF), rectangular pieces of borosilicate glass samples were suspended separately in 50 ml of freshly prepared SBF. The details of the composition of the SBF are presented in Table 1. The freshly prepared solutions were kept at 37°C in an incubator at static condition for 1 and 2 weeks. The samples were dried inside a desiccator after removing from the SBF, and then the infrared reflection spectra were measured using FT-IR spectrometer (type Jasco FT-IR-430, Japan) with diffusive reflection attachment (model DR-400c). The samples were measured in the wavenumber in the range from 4000-450 cm⁻¹ at a resolution of 2 cm⁻¹ and scanning speed 2 mms⁻¹.

#### 2.3 Procedure for preparation of simulated body fluid (SBF)

For the preparation of fresh 1000 ml SBF, 950 ml of distilled water was introduced into 1000 ml plastic (polyethylene) beaker. Heat the beaker at 37°C and dissolve 6.057 g and adjust the pH of the solution by addition of 6.057 g and adjust the pH of the solution by

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**Table 1— Reagents for preparation the simulated body fluid (SBF)**

<table>
<thead>
<tr>
<th>Order</th>
<th>Reagent</th>
<th>Amount in grams</th>
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<tr>
<td>1</td>
<td>NaCl</td>
<td>7.996</td>
</tr>
<tr>
<td>2</td>
<td>NaHCO₃</td>
<td>0.350</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>0.224</td>
</tr>
<tr>
<td>4</td>
<td>K₂HPO₄·3H₂O</td>
<td>0.228</td>
</tr>
<tr>
<td>5</td>
<td>MgCl₂·6H₂O</td>
<td>0.305</td>
</tr>
<tr>
<td>6</td>
<td>IM HCl</td>
<td>40 ml</td>
</tr>
<tr>
<td>7</td>
<td>CaCl₂</td>
<td>0.278</td>
</tr>
<tr>
<td>8</td>
<td>Na₃PO₄</td>
<td>0.071</td>
</tr>
<tr>
<td>9</td>
<td>(CH₃OH)₂CNH₂</td>
<td>6.057</td>
</tr>
</tbody>
</table>
adding IM HCl at 7.4 at 37°C. Add the reagents cited in Table 1 one by one in the order given gram 1 to 8 with vigorous stirring. Then add de-ionized water to complete the mark of the beaker to 1000 ml and keeping the PH at 7.4. The SBF should be used within 30 days after preparation and being kept at 5-10°C in a refrigerator.

2.4. Electrical measurements

LCR meter type AG-4311B Ando Electric LTD (Japan) was used for the frequency range between 0.1 and 100 kHz. The capacitance C, the loss tangent tan D and ac resistance were measured directly from the bridge, from which the permittivity 8' and dielectric loss 8" and also $R_{ac}$ were obtained.

The cell used is a parallel plate circular condenser made of silver of 1mm diameter attached to a movable micrometer. The cell was calibrated using standard materials (air $\varepsilon=1$, tritolul air $\varepsilon=2.54$ and glass $\varepsilon=7$) according to the method discussed before. The borosilicate glass samples of the undoped and that doped with different transition metal ions were molded into discs of 2 mm diameter and equidistant thickness (0.2-0.6mm).

3 Results and Discussion

3.1 Infrared reflection spectra

Infrared spectra of both silicate or borate are, generally, agreed upon. The IR spectra are accepted to reflect the basic characteristic groups in the structure of these glasses. The fundamental building block in silicate glasses is the SiO$_4$ tetrahedral unit, and in pure SiO$_2$ all of the oxygen atoms are shared between two tetrahedral, forming a fully polymerized network. Alkali or alkaline earth cations act as network modifiers, breaking bridging oxygen bonds to form non-bridging oxygen atoms (NBOs) and residing in sites interstitial to the tetrahedral network in the vicinity of the negatively charged NBOs. B$_2$O$_3$ can form by itself a glass consisting of triangular boron-oxygen units mostly condensed as boroxol groups. When alkali or divalent oxide is added to B$_2$O$_3$, part of the boron is progressively transformed to tetrahedral coordination until certain limit depending on various parameters.

Borosilicate glass is, therefore, considered to be a composite glass composed of three network forming units, namely SiO$_4$, BO$_3$ and BO$_4$ groups in different proportions depending upon the glass composition. It is expected that infrared spectroscopy of such borosilicate glass should reveal characteristic

Fig.1— Infrared reflection spectra of the borosilicate glasses undoped and doped with different transition metal ions before immersion in SBF

Fig.2— Infrared reflection spectra of the borosilicate glasses undoped and doped with different transition metal ions after immersion in SBF for 1 week at 37°C
absorption bands due to the collective vibrations of the three different mentioned structural groups. The realization and interpretation of the infrared spectra could be carried out in agreement with the concept adopted by Tarte and Condrate about the independent vibrations of different groups. The various vibrations of different groups nearer to each other may therefore assume a composite one.

Figures 1-3 show the infrared reflection spectra for the studied borosilicate glasses before and after the immersion in SBF for 2 weeks at 37°C.

The spectra of all samples before immersion show a very broad band cited at about 1079 cm\(^{-1}\) overlapped with another band at about 1013 cm\(^{-1}\) which are due to the Si-O-Si asymmetric stretching of bridging oxygen atoms within the tetrahedral and also, the B-O stretching vibration\(^{37,38}\). Also there are four small bands at about 900 and 771, 477 and 460 cm\(^{-1}\) which are correlated to the B-O-Si stretching, Si-O-Si symmetric stretching of bridging oxygen atoms between the tetrahedral and due to the Si-O-Si and O-Si bending vibration\(^{37,38}\), respectively.

After immersion of the borosilicate glasses in SBF for 1 week at 37°C, the infrared reflection spectra show no obvious changes in the positions of the bands that are observed before immersion and this may indicate that there is no change on the surface of the studied glasses after 1 week of immersion.

After two weeks of immersion in SBF solution at 37°C, the infrared reflection spectra show obvious changes especially in region (550-650cm\(^{-1}\)), where there are two new separate bands cited at about 592 and 605 cm\(^{-1}\). these two bands are accepted to be due to the formation of surface crystalline hydroxyapatite layer. The intensities of these two bands are observed to vary with the type of the transition metal ion that was added to the glass batch. The intensities show relatively higher values when CuO, MnO\(_2\), NiO or TiO\(_2\) were added, and lower values when Cr\(_2\)O\(_3\) was added. But in the case of the addition of either CoO or V\(_2\)O\(_5\) two bands at about 592 and 605 cm\(^{-1}\) could not be identified as separate peaks but there is overlapping between the two bands and this can be explained by assuming that the layer formed on the glass surface is still amorphous calcium phosphate and is not matured or converted to the crystalline form yet.

These changes in the infrared reflected spectra obtained from the surfaces of the borosilicate samples upon immersion in SBF can be also be correlated with the proposed stages of formation of the hydroxy carbonate apatite by Hench\(^{3}\) and further justified by El-Batal et al\(^{39}\). However, it is not obvious from the experimental IR data, the exact role of each transition metal oxide. Most of these TM oxides are known to play a role of nucleating agents in the crystallization of different glass systems\(^{40,41}\). The equivalent per cent added of the TM oxides cannot aid in the judgment of the efficiency of the TM oxides in initiating the crystallization of HCAp which is clear in the IR spectra. It is of much importance to consider that Kokubo et al\(^{42,43}\) have shown that the presence of TiO\(_2\) especially in the anatase form aids in the anatase form aids in the formation of apatite. They consider that the bioglass releases Ca\(^{2+}\), Na\(^+\) or K\(^+\) ions from its surface via ion exchange with the H\(_3\)O\(^+\) ions in the SBF to form Si-OH or Ti-OH groups on their surfaces. Water molecules in the SBF then or simultaneously react with the Si-O-Si or Ti-O-Ti bond to form additional Si-OH or Ti-OH groups on their surfaces. Water molecules in the SBF then or simultaneously react with the Si-O-Si or Ti-O-Ti bond to form additional Si-OH or Ti-OH groups. The Si-OH and Ti-OH groups formed induce apatite nucleation, and the released Ca\(^{2+}\), Na\(^+\) or K\(^+\) ions accelerate apatite
nucleation in the fluid. Once the apatite nuclei are formed, they can grow spontaneously by consuming the calcium and phosphate ions in the surrounding fluid because the body fluid is highly saturated with respect to the apatite. However, it has been suggested that functional groups are determined not by their composition alone, but in a complicated faction that is dependent on their concentration and structural arrangements. It seems that further studies are still needed to justify the proper mechanism for each transition metal ion separately.

Hench had introduced a patented bioactive borosilicate glass Code No. 45BSS5 which contains 15wt% B$_2$O$_3$ replacing SiO$_2$. The bioactivity of alkali borosilicate glasses was examined by some researchers. They noted that sodium borosilicate glasses required relatively long induction period for apatite formation than Hench's bioglass of the following main constituent: 30 Na$_2$O, 20 B$_2$O$_3$, 50 SiO$_2$, resulted from the largest fraction of Si atoms bonding to two bridging oxygen atoms.

3.2 Electrical parameters

It is, generally, accepted that the conduction mechanism in silicate glasses is carried our by ionic motion of the monovalent alkali ions. The monovalent alkali ions are situated in silicate glasses in interstitial positions after they break out the silicon-oxygen bonds. Monovalent alkali modifiers are easily detached to migrate and the conduction is easier with the decrease of the ionic size of the alkali cations. With the introduction of divalent oxides, the silicate glass is chemically improved and the conduction becomes lower, this behaviour is considered to be due to the blocking or retardation of the conduction paths of the monovalent alkali ions due to the interference from mixed cations with different charges and the presence of other ions with relatively larger ionic sizes possessing relatively lower mobility.

The basic studied glass is a borosilicate type, which is known to have a relatively compact structure than ordinary binary alkali silicate. The introduction of boric oxide produces surplus BO$_3$ and BO$_4$ structural building units together with SiO$_4$ units. Also, the alkali cations are firmly attached to BO$_4$ tetrahedra to compensate for the surplus negative charges and are not freely situated as in alkali silicate. Therefore, it is expected that the conduction mechanism is relatively lower than with alkali silicate glasses.

Figure 4 shows the variation of the permittivity and dielectric loss for borosilicate glass with different transition metals as a function of frequency dielectric loss for borosilicate glass with different types of transition metal oxides (Cr$_2$O$_3$, V$_2$O$_5$, CoO, NiO, TiO$_2$, MnO$_2$, Fe$_2$O$_3$, and CuO). The measurements were carried out over a frequency range 100 Hz - 100 kHz, at room temperature (25°C).

Fig.4 shows that the values of ε decrease slightly with increasing the applied frequency, which shows anomalous dispersion. It is also noticed that the values of ε for the investigated samples at the whole range of the tested frequencies are slightly higher than those for the blank glass sample. This is properly related to the addition of different transition metals in a small amounts. Also it is obvious that the values of the permittivity of the samples containing oxides of Cr, Ni and V are slightly the same and this may be due to the similarity in the splitting order of the ions of such oxides. Figure 4 shows also the dependence of ε'' upon the applied frequency for the above investigated systems. The values of ε'' for transition metals doped glasses are found to be higher than those of blank undoped glass, which could be attributed to the high conductivities due to the addition of dopant transition metal oxides. From Fig.4, it is clear that the values of ε'' in the lower frequency range seem to be high indicating the presence of dc conductivity.
Figure 5 shows the dependence of $\varepsilon'$ and $\varepsilon''$ for the investigated glasses after immersion in SBF upon the applied frequency. It is found that the values of $\varepsilon'$ and $\varepsilon''$ for the investigated samples are lower than those for blank glass. This is naturally related to the formation of hydroxyl apatite bonds on the surface of the glass matrix which leads to a decrease in the freedom of the movements of conduction within and between transition metals and glass matrix. Therefore, a relatively lower permittivity was obtained when compared with that of blank glass. Also the development of hydroxyl apatite on the surface of the glass matrix in the presence of different transition metal will he expected to decrease the value of dielectric loss for the whole investigated sample than that of the corresponding blank.

By comparing the variation of permittivity and dielectric loss of the investigated samples before and after immersion in Figures 4 and 5, it is evident that in the case of Fig. 5 the spectrum is more broad due to the presence of more than one process which is developed as a result of the addition of dopant TM oxide and the formation of HA/glass complex.

From the values of electrical resistance obtained for the different investigated systems, the $dc$ conductivity was calculated and given in Table 2. The dielectric losses due to the $dc$ conductivity data were calculated according to the following equation\(^{20}\), and subtracted from the experimental $\varepsilon''$ value as shown in Figure 5.

\[
\varepsilon''_{dc} = \left(9 \times 10^{11} \times 4\pi \sigma \right) / \omega \quad \ldots(1)
\]

where $\omega$ is the applied frequency in Hz.

A number of researchers\(^{22,23}\) have investigated the change in electrical conductivity of alkali-silicate glasses associated with the addition of different transition metals. A variation in conductivity is obtained depending on the transition metals which are presented in Table 2. the effectiveness of the transition oxides in varying the conductivity has been obtained. The interpretation of this effect is that the divalent or polyvalent ions block the conduction paths of the alkali ions depending on its size\(^{46}\). It is also possible that the divalent and monovalent ions coordinate with the mutual oxygen ions in oxides, thus maximizing the charge distribution in the glass.

The motion of alkali ions can, however, be suppressed in silicate and borate glasses by addition of calcium, barium or lead ions\(^{47}\). Ionic conduction becomes negligible since it is suggested that the highly immobile divalent ions block migration channels. Transition metals exhibit two valence states or more except Co and Ni ions which are always in a divalent state. Glasses containing large amount of transition metal ions are really semiconducting materials because of the presence of TM ions in two different valence states. It has been postulated that conduction takes place by a hopping process\(^{46-48}\).

The studied base glass is a borosilicate to which is added 0.1% of one of the transition metal oxides (Ti$\rightarrow$ Cu) as a dopant. The borosilicate glass possesses a compact structure and the migration of the alkali ions in this glass is lower than that in sodium silicate glass. The addition of a transition metal oxide glass dopant is assumed to introduce electronic conduction mechanism even in a low scale beside the already existing ionic conduction mechanism\(^{48}\). In other words, the glass is believed to contain some mixed ionic and electronic conduction mechanisms.
similar mixed conductivity was found by Barczynski and Murawski\textsuperscript{49} in sodium iron phosphate glasses but the TM content in their glasses was high (30-50 mol%).

The data of $\varepsilon''$ after subtraction of dc losses show a well defined absorption region and can be analysed according to Havriliac Nagami equation\textsuperscript{50}.

$$\varepsilon^*(\varpi) = \varepsilon + \frac{\varepsilon_\infty - \varepsilon_1}{1 + (\varpi \tau)^\alpha}$$

$0 \leq \alpha \beta \leq 1$

Examples of the analysis are given in Figures 6 and 7 for blank and co-doped glasses, respectively before and after immersion in SBF. From Figures 6 and 7, it is found that the dielectric spectra give one absorption region before immersion and two absorption regions after immersion. The process before may be correlated with the interfacial polarization of the different oxides forming the glass matrix and the molecular rotation. For the second process obtained in the spectra after immersion which is expected to be related to the development of HCAp layer on the surface of a bioactive borosilicate glass. The data in Table 2 confirm these interactions where it is found that the second relaxation time varies depending on the different transition metals and the ability of these metals to mostly initiate the formation of HA crystalline layers. These data are confirmed by IR spectroscopy.

The present investigation follows up the possible changes or reactions which are expected to be formed between the different transition metal ions in glass matrix and SBF through the dielectric relaxation.

<table>
<thead>
<tr>
<th>Before</th>
<th>$\sigma \times 10^{15}$ S/m</th>
<th>$\tau_1$ sec</th>
<th>$\Delta\varepsilon_1$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
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<td>Vv</td>
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<td>0.1114</td>
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<td>0.6</td>
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<td>Ni</td>
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<td>0.1074</td>
<td>0.3</td>
<td>0.6</td>
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<tr>
<td>Ti</td>
<td>14.1</td>
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<td>0.1332</td>
<td>0.3</td>
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<td>Cu</td>
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<table>
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<th>$\Delta\varepsilon_2$</th>
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<tbody>
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<tr>
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</table>

Fig.6 — Absorption curve of blank sample before and after immersion in SBF. The data are fitted by Havriliac and conductivity term.
measurements especially $t_2$ which has a particular interest in this study. The values of the dielectric parameters obtained from the analysis are listed in Table 2. From this study, it could be concluded that the dielectric parameters of transition metals doped-borosilicate glasses samples forming a surface HA layer are dependent on the type of metal ions in the sample and the valence of these ions which are virtually affecting the conductivity of the sample. Further work are still required to justify the effect of each transition metal with increasing concentration separately on the formation of surface HA layer and interrelation to the mentioned parameters.

4 Conclusion

Studies on the bioactivity of transition metals (Ti$\rightarrow$Cu)–doped borosilicate glasses reveal the formation of hydroxyapatite surface layer after immersion in SBF solution for 2 weeks. Infrared reflection spectra show variations according to the type of TM. Electrical measurements reveal the same behaviour. Interpretation of the bioactivity data are correlated with the processes of corrosion steps and the primary formation of silica gel and amorphous calcium phosphate which finally crystallized as known by the characteristic IR peaks. The electrical data are also explained on the effect of the formation of HAp layer and the possible mixed ionic and electronic mechanisms due to the addition of transition metal oxides.

References

17 Oonishi H, Kushitani S, Yasukawa E, Iwaki H, Hench, L L,