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## Bioactivity Assessment of Some Borate Glasses Containing Copper.

Issam H Al-Ahdali\*, IS Ali, and MA El-Bakary.

Physics Department, Faculty of Applied Science – Umm-A-IQura University, Makkah, Saudia Arabia  
Occupational Health, Faculty of Public Health and Health Informatics - Umm Al-Qura University. Makkah, Saudia Arabia  
Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt.

### ABSTRACT

Modified bioglasses were prepared by full replacement of  $\text{SiO}_2$  in Hench's patented bioglass by  $\text{B}_2\text{O}_3$  together with samples containing successive additions of  $\text{CuO}$  (0.2 to 4%). The bioactivity behavior of the prepared borate glasses was analyzed by immersing the glasses in simulated body fluid (SBF) and measuring the appearance of hydroxyapatite (HA) through combined FTIR spectra, X-Ray diffraction and Scanning (SEM) techniques. After immersion, FTIR spectra reveal the appearance of the far IR split band with two peaks at 550-570 and 620-650  $\text{cm}^{-1}$  after immersion of the glasses in SBF solution. It is observed that the progressive increase of  $\text{CuO}$ , increases the intensity of this characteristic peaks which are due to the formation of calcium phosphate (hydroxyapatite) and this increase ceases after 1%  $\text{CuO}$  reaching to constancy or slight decrease. X-Ray diffraction analysis supported the FTIR results. Also, SEM images show the appearance of the modular texture known for hydroxyapatite.

**Keywords:** Borate, Bioglass,  $\text{CuO}$ , FTIR, XRD, SEM

*\*Corresponding author*

## INTRODUCTION

In 1971, the concept of bioactive glassy material was announced by Hench et al [1]. Since then, the field of bioactive glasses and glass-ceramics has expanded enormously to include many new compositions and systems of glasses, glass ceramics and ceramics [2-10]. These compositions include silicate, phosphate and borate glasses in addition to their glass ceramic derivatives.

Silicate bioactive glasses such as Hench patented bioglass (45S5) commonly convert slowly and incompletely to amorphous calcium phosphate or hydroxyapatite (HA) surface material when reacted with body fluids in case of in-vivo test or simulated body fluid (SBF) in case of in-vitro test and the presence of silicon ions remaining is questionable [2].

Bioactive phosphate glasses are almost totally dissolved being similar to bony materials in composition [5]. Borate-based biomaterials (glass or glass-ceramics) have been developed and tested for biomedical applications [4, 8]. It has been reported that the release of controlled amounts of boron during degradation of these borate-base biomaterials can have some beneficial effects on bone repair, since small concentrations of boron have been found to be promising for bone metabolism [11]. Furthermore, boron can also quickly dissolve in the body fluid and be excreted through urine [12].

In the course of this work, the first objective is to characterize the bioactivity (or bone-bonding ability) of some prepared borate glasses based on the modification of Hench bioglass by replacing completely  $\text{SiO}_2$  by  $\text{B}_2\text{O}_3$  and subjecting them to immersion for prolonged times in SBF. Also, the study is extended to investigation of the corrosion behavior of the prepared glasses. The overall work comprises FT infrared absorption measurements before and after immersion and supported by both x-ray diffraction (XRD) and scanning electron microscopy (SEM). Addition of CuO (0.2, 1, 2, 4%) were added to investigate their effects on the bioactivity because of its beneficial effects on inhibiting bacteria growth.

## EXPERIMENTAL

### Glass Preparation

Samples of nominal composition (45 $\text{B}_2\text{O}_3$  - 24.5 $\text{Na}_2\text{O}$  - 24.5 $\text{CaO}$  - 6 $\text{P}_2\text{O}_5$ )wt% together with some samples of CuO-doped glasses where copper was added as additive (0.2, 1, 2 and 4 gm/batch) were prepared in the present study (Table 1). Reagent laboratory grade  $\text{H}_3\text{BO}_3$  (99% from Nasr Lab., Egypt, Fe 10ppm), ammonium dihydrogen phosphate (, Fe 0.01%) and CuO (99.0% BDH, England, Fe 0.05%), while  $\text{Na}_2\text{O}$  and  $\text{CaO}$  were introduced in the form of their respective anhydrous carbonates.

Table 1

Sample	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{P}_2\text{O}_5$	CuO
BioBGCu0	45.0	24.5	24.5	6.0	0.0
BioBGCu0.2	45.0	24.5	24.5	6.0	0.2
BioBGCu1	45.0	24.5	24.5	6.0	1.0
BioBGCu2	45.0	24.5	24.5	6.0	2.0
BioBGCu4	45.0	24.5	24.5	6.0	4.0

The weighed batches were melted in platinum crucibles at 1050 °C for 2 hours. The melts were rotated at intervals of 30 minutes apart to ensure the melt homogeneity. Homogenized melts were cast into warmed stainless steel molds of the required dimensions and the prepared samples were immediately transferred to a muffle furnace regulated at 380 °C for annealing and removing thermal stresses. The annealing muffle was switched off after 1 hour and left to cool to room temperature at a rate of 25 °C/h.

### Structural analysis of bioglasses using FTIR analysis

Fourier transform infrared (FTIR) absorption spectra of the glasses were measured at room temperature (~ 20°C) in the wavelength range 2000-400  $\text{cm}^{-1}$  using an FTIR spectrometer (Nicolet i10). Fine powders of the samples were mixed with KBr in the ratio 1:100 for quantitative study and the mixtures were

subjected to a load of 5 tons/cm<sup>2</sup> in an evacuable die to produce clear homogeneous discs. Then, the IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack. The measurements were taken for the studied samples before and after immersion in the SBF solution.

### Structural analysis using scanning electron microscopy

Scanning electron microscopic (SEM) investigations were performed on glass samples at room temperature using an SEM Model Philips XL 30 attached with EDX Unit, accelerating voltage 30 K.V., magnification 10× up to 400,000. All samples were coated with gold for morphological investigations.

### X-ray diffraction analysis

The crystallinity of the samples after immersion were analyzed by X-ray diffraction in order to identify the structural changes after immersion in the SBF solution. The glass samples were ground and the fine powder was examined using a diffractometer adopting Ni-filter and Cu-target. The X-ray diffraction patterns were obtained using a Philips PW 1390 X-ray diffractometer.

## RESULTS

### FTIR spectra of glasses before immersion

Figure 1 shows the FTIR absorption spectra of the studied glasses. The base soda lime phosphoborate glass (BioBGCu0) reveals the following IR spectral characteristics:

- a) Three successive small far IR bands at 410, 626 and 717 cm<sup>-1</sup>.
- b) A strong broad band with two peaks at 872 and 1027 cm<sup>-1</sup>.
- c) The second strong broad band with slight higher intensity than the preceding one and with two peaks at 1407 and 1505 cm<sup>-1</sup> followed by a band at 1634 cm<sup>-1</sup>.
- d) Two small peaks around 2850 and 2927 cm<sup>-1</sup>.
- e) A strong and broad near IR band centered at 3439 cm<sup>-1</sup>.

While the following spectral features characterize the FTIR spectra (Fig. 1) of the glasses containing CuO (BioBGCu0.2, BioBGCu1, BioBGCu2, BioBGCu4):

- f) The relative intensity of the broad bands changes with addition of CuO,
- g) The first far IR peak around 410 cm<sup>-1</sup> disappears when all CaO are replaced with CuO and
- h) The intensity of the broad band at 3439–3500 cm<sup>-1</sup> decreases with replacement of CaO with CuO (BioBGCu4).
- i) A new small band appears at 1230 cm<sup>-1</sup> with replacement of CaO with CuO (BioBGCu1), (BioBGCu2) and (BioBGCu4).

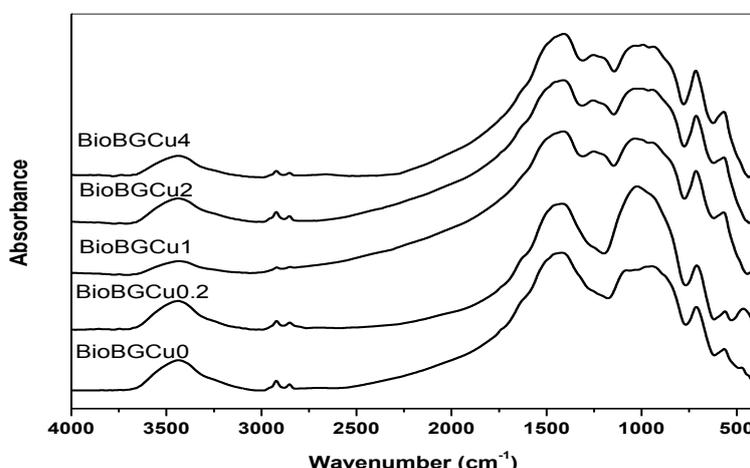


Figure 1: FTIR absorption spectra of prepared glasses before immersion in SBF solution for two weeks

### FTIR spectra after immersion

Figure 2 illustrates FTIR spectra of the studied glasses after immersion in SBF solution for two weeks. Careful inspection of the IR spectral curves indicates that distinct variations are observed and identified in the obtained results and can be summarized as follows:

- The far-IR bands within the wavenumber range at  $400\text{-}700\text{ cm}^{-1}$  are highly distinguished by sharp peak and a new distinct band with two connected peaks at  $564$  and  $602\text{ cm}^{-1}$ .
- The broad absorption extending from about  $900$  to about  $1250\text{ cm}^{-1}$  exhibits high intensification as revealed by the very high broad band with a sharp peak at  $1031\text{ cm}^{-1}$ .
- The broad absorption extending from about  $1250$  to about  $1580\text{ cm}^{-1}$  decrease in intensity after immersion but the observed band exhibits four peaks at  $1330$ ,  $1360$ ,  $1427$  and  $1480\text{ cm}^{-1}$ .
- A distinct medium band is identified at  $1650\text{ cm}^{-1}$ .
- The near-IR very broad bend extending from about  $2750$  to  $3750\text{ cm}^{-1}$  with distinct broad peak at  $3440\text{ cm}^{-1}$  and two small kinks at  $2853$  and  $2922\text{ cm}^{-1}$ .
- The glasses containing increasing CuO contents reveal that on reaching  $1\%$  CuO, the far IR band with two split peaks is observed to be highly increase and with more CuO ( $2\%$ ), this band returns to its intensity for the undoped or that with  $0.2\%$  CuO.

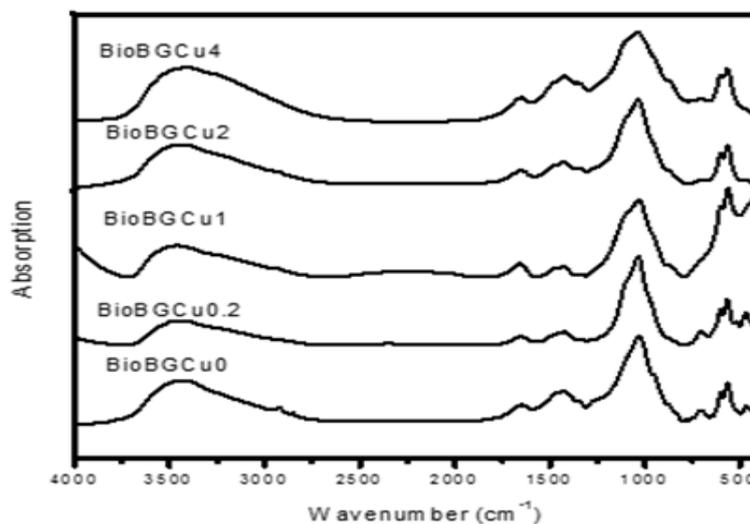


Figure 2: FTIR absorption spectra of prepared glasses after immersion in SBF solution for two weeks

### DISCUSSION

#### Interpretation of the FTIR spectral results

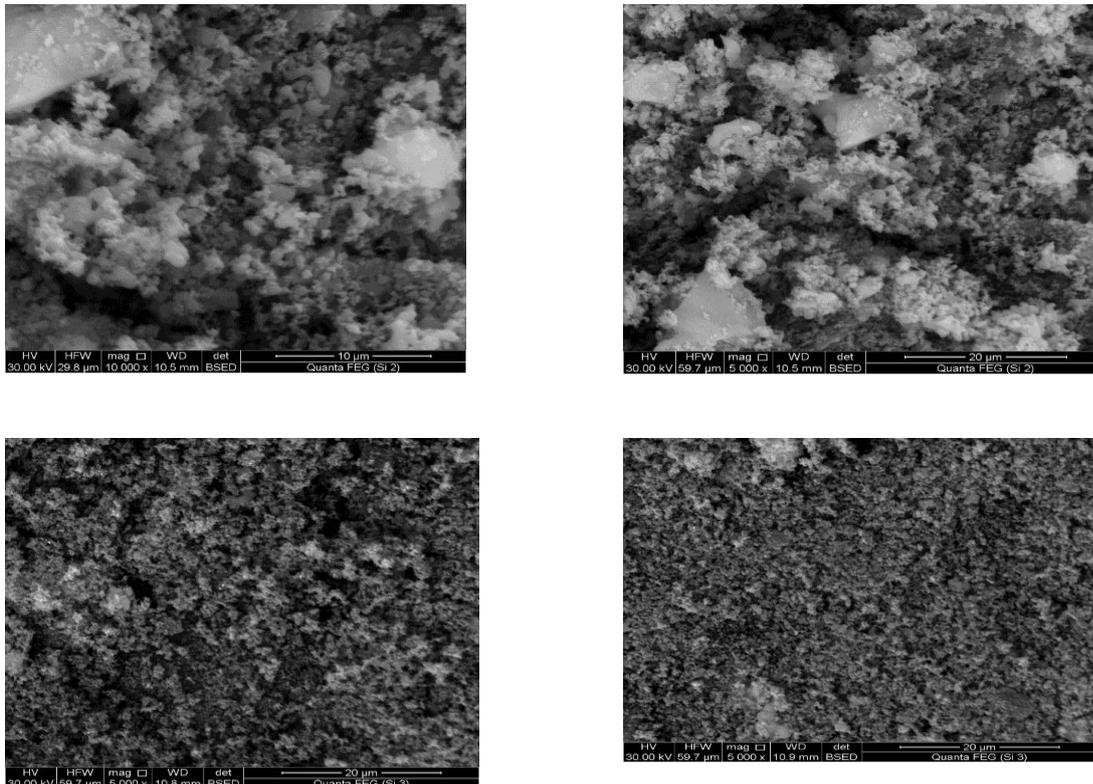
Infrared spectroscopy is one of the most efficient tool to identify the detailed structural groups in glasses which X-ray diffraction analysis fails to explore as happened with crystalline materials [13-15]. Also, FTIR can be applied to specify the route of corrosion mechanism in glasses and to confirm the bone-bonding ability in bioactive glasses [16, 17]. Borate glasses belong to distinct system which possess rich chemistry in having the ability to have both triangular and tetrahedral borate units varying in ratio according to the percent of other partner oxides (alkali oxide, alkaline earth oxide).

The IR results can be interpreted on the following basis:

- It should be born in mind that the transformation of ceases after certain percent and the excess of modifier oxide brings the formation of the nonbridging oxygens.
- It is expected that the formation constitution of the studied glasses contains both triangular and tetrahedral borate units.

- c) It is accepted that the vibrational modes of the triangular and tetrahedral borate units are active in different wave numbers [18]. The triangular borates are vibrating at  $1200-1600\text{ cm}^{-1}$  which the tetrahedral borates are active in the range  $800-1200\text{ cm}^{-1}$ .
- d) Before immersion, the IR spectra within the two different ranges reveal almost equal intensities for both the ranges which denote approximately equivalent percents of  $\text{BO}_3$  and  $\text{BO}_4$  units.
- e) After the immersion in SBF solution for two weeks, it is observed that the intensity of the first broad absorption banding the range  $800-1200\text{ cm}^{-1}$  is higher than the second broad absorption in the range  $1250-1600\text{ cm}^{-1}$ .
- f) This result indicates that  $\text{BO}_3$  groups are reached or dissolved in the immersion liquid faster than the dissolution of the  $\text{BO}_4$  groups. This can be realized by referring that the boron atoms are firmly and equally bonded in  $\text{BO}_4$  groups within four directions with the nearby alkali (or divalent) ions firmly attached to compensate for the surplus negative charge. On the other hand, the borons in  $\text{BO}_3$  groups are not equally bonded and thus easily dissolved.
- g) The resolution of the distinct characteristic band with two-split peaks at about  $(560-566\text{ and }601-606\text{ cm}^{-1})$  after immersion is correlated with the formation of calcium phosphate as it is known to be an indication or characteristic of the bone-bonding or bioactivity of the glass.
- h) The introduction of  $\text{CuO}$  with 1% observed to increase the resolution and intensity of the mentioned far-IR band with two peaks at about  $550-601\text{ cm}^{-1}$  to the highest extent and then intensity returns to lower level. This refers to the initiation of copper ions up to 1% to the bioactivity of this system studied.
- i) Previous similar results on the effect of  $\text{TiO}_2$  (specially anatase phase) on the bioactivity behavior of phosphate glass ceramic have been reached [19]. The presence of maximum 1.5%  $\text{TiO}_2$  has been observed to promote in-vivo dissolution of the phosphate bioglass-ceramic into the tissues of femurus of a rabbit. Higher concentration of  $\text{TiO}_2$  causes a reverse effect.

**Interpretation of the SEM results**



**Figure 3: SEM of prepared glasses before immersion in SBF solution for two weeks**

SEM micrographs of the powdered glass surfaces before and after immersion in SBF solution for two weeks are shown collectively in Fig. 3. The micrograph of the glass before immersion is characterized by a nearly smooth surface but contains some undefined grains with gradually appearance of cotton-like growths

or nodules on the surface of the sample after immersion the glass in SBF solution. These cotton-like growths or nodules are due to the formation of the apatite crystals as identified by X-ray diffraction analysis [12]

**Interpretation of the X-ray diffraction analysis results**

Figure 4 (a, b) shows the X-ray diffraction patterns of the prepared bioglasses before and after being immersed in SBF solution for two weeks. All as prepared glasses (figure 4-a) was amorphous in nature and reveals no crystalline peaks indicating and confirming the amorphous structure of all samples with no change in its nature before and after successive addition of Copper metal oxide (CuO) and transformed to material that contains at least three different crystalline phases depending on the composition (figure 4-b); ternary calcium borate crystalline phases as the main phase and binary calcium or sodium borate phases. In addition to monoclinic borax  $B_4O_5(OH)_4(Na_2(H_2O)_3)$  and hydroxyapatite phase with crystallinity about 52% as calculated using a computer program (Materials Studio 4.4) this results was supported by the SEM micrographs.

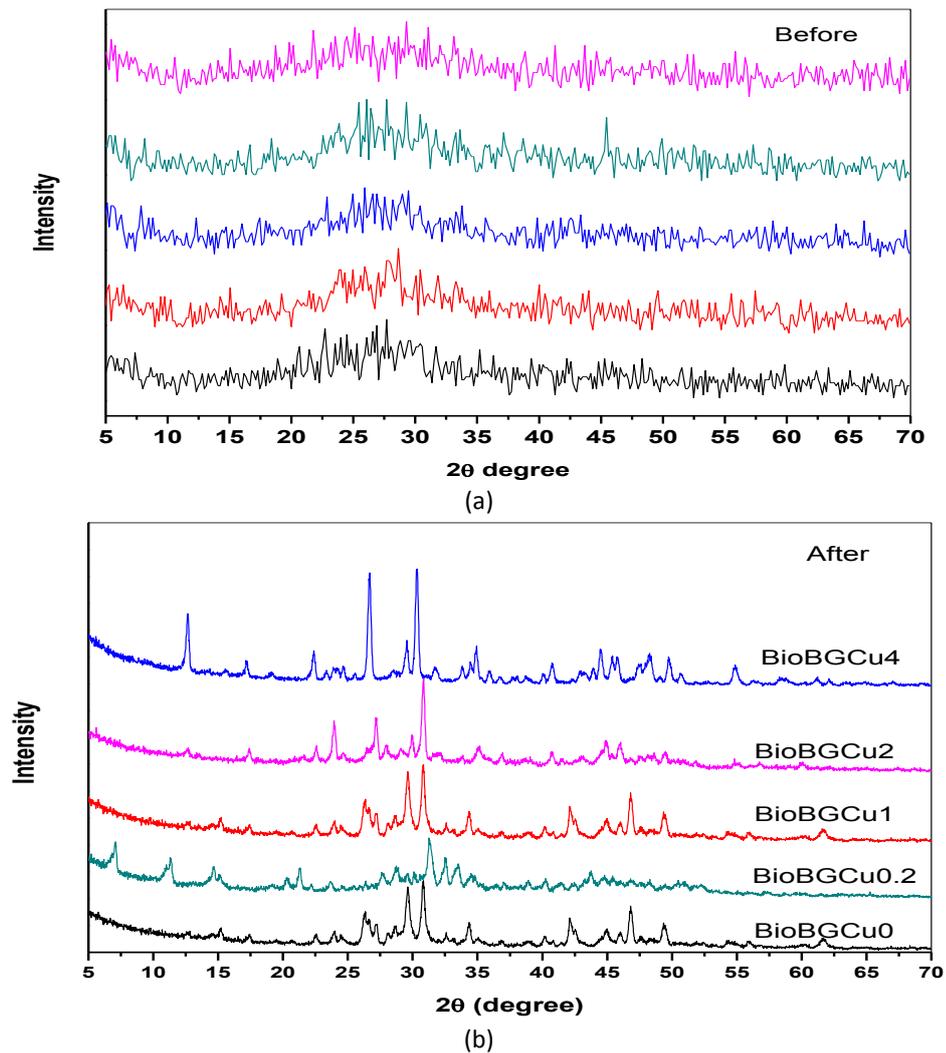


Figure 4: x-ray diffraction pattern before and after immersion for 2 weeks

**CONCLUSIONS**

Quarterly modified borate bioglasses were prepared by full replacement of  $SiO_2$  in Hench's patented bioglass by  $B_2O_3$  together with samples containing variable concentrations of CuO (0.2 to 4%). The bioactivity behavior of the prepared borate glasses was analyzed by immersing the glasses in simulated body fluid (SBF) and measuring the appearance of hydroxyapatite (HA) through combined FTIR spectra, X-Ray diffraction and selected samples by scanning electron microscopy (SEM) techniques. After immersion, FTIR spectra reveal the

appearance of the far IR split band with two peaks at 550-570 and 620-650  $\text{cm}^{-1}$  after immersion of the glasses in SBF solution. It is observed that the progressive increase of CuO, increases the intensity of this characteristic peaks which are due to the formation of calcium phosphate (hydroxyapatite) and this increase ceases after 1% CuO reaching to constancy or slight decrease. This phenomenon was approved by XRD data. X-Ray diffraction analysis supported the FTIR results. Also, SEM images show the appearance of the modular texture known for hydroxyapatite.

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