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Metallurgical Behavior and Biocompatibility of Boron Trioxide on the Bioactive Glasses

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Abstract

Bioactive glass is explicitly accredited for its marvelous biological and bioactive tendency. Also, this is importantly proclaimed for its potential to generate bonds with the bone. There are numerous applications of bioactive glass, one of the noteworthy applications is the reproduction of bone grafts that is applied for both orthopedic and periodontal function. Bioactive glass based on silica designated 1393 bioactive glass [Composition wt.% $53SiO_2$ - $12K_2O$ - $6Na_2O$ -5MgO-20CaO- $4P_2O_5$] has been acquired from the 45S5 bioactive glass configuration, Bioactive glass based on silica designated 1393 bioactive glass [Composition wt.% $53SiO_2$ - $12K_2O$ - $6Na_2O$ -5MgO-20CaO- $4P_2O_5$] has been acquired from the 45S5 bioactive glass configuration but the percentage of SiO_2 and network modifiers, like K_2O and MgO, are comparatively higher in 1393 bioactive as a comparison to 45S5 bioactive glass, In the medical field, mostly 1393 bioactive glass is also considered useful. In this study, the outcome when boron trioxide (B_2O_3) is added to 1393 bioactive glass has been explained. The preparation of boron trioxide substituted bioactive glass. FTIR spectrometry, SEM, and most important bioactivity of the samples of glass were inspected by a test called in vitro in presence of Simulated Body Fluid (SBF). The results indicate that when silica is replaced with boron trioxide in 1393 bioactive glass improved its biocompatibility, density, and mechanical behavior.

Keywords: Bioactive Glass, Boron Trioxide, Biocompatibility, Flexural Strength, Microhardness

1.0 Introduction

There are different Bio-glass[®] one of them is known as bioceramics¹. Defects of bone that come in the category of non-healing and injured or infected parts of the musculoskeletal system be revamped and permeated by the bioceramic. Bioceramic composites² can be produced by sintering), biomaterials are found in various forms as bioinert (composition of alumina and boron trioxide), bioactive (form hydroxyapatite layer), resorbable (composition of tricalcium phosphate), or porous for tissue growth (hydroxyapatite-coated metals, alumina Bioactive Glasses (BG) have been developed in various

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forms over the past years. There are numerous natures of Bioactive Glasses (BG) but the topmost ability is to generate strong bonds with a bone when it comes in contact with the bone it develops a layer of hydroxyapatite on the surface of the bone³. Bioactive Glasses (BGs) such as "45S5 Bio-glass[®]" (24.5 wt% CaO, 6 wt% P_2O_5 , 45 wt% SiO₂ 24.5 wt% Na₂O₃) and "1393" (53 wt% SiO₂, 6 wt% Na₂O, 12 wt% K₂O, 5 wt% MgO, 20 wt% CaO, and 4 wt% P_2O_5) compositions have been broadly used for applications of bone tissue engineering. Hench *et al.*²⁻⁴ inspected the cause of the bonding mechanism with synthetic material in vitro and found these occur because of chemical responses that arise on the surface of the

glass. These chemical responses are the main cause of the bonding of bone tissue with implants; Therefore diseased or injured parts of the human cartilage⁵ can be replaced. A number of researches have been done and also going on for the establishment and improvisation of glass-ceramics and bio-glasses, added with various ions for instance Ti, B, Zr, Zn, Sr, Mg, Li, K, and Fe, for the reason that they show differently tendency for the proliferation of the osteoblastic cell and for mineralization of bone⁶⁻¹². In this work boron trioxide (B_2O_2) is replaced in place of SiO₂ in 1393 bioactive glass is fabricated by controlled crystallization of bioactive glasses. The B₂O₃ ceramic has outstanding strength including fracture toughness which is why it is extensively utilized as a substrate in hard tissue applications. A number of research articles recommended that boron trioxide has good in the field of chemical qualities and stability of dimensions, and mechanical properties and it represents a feature of bioinert materials. In previous research¹³⁻¹⁵. Resistance against hydrolysis can be minimized by increasing the percentage of trioxide of boron in the glass formation. (Order of countering for hydrolysis: B-O-B<Si-O-B<Si-O-Si)¹⁶.

2.0 Materials and Methods

2.1 Composition and Glass Preparation

The source of SiO₂ was in the form of Fine-grained quartz, Anhydrous calcium carbonate (CaCO₃) and sodium carbonate (Na₂CO₃) was used to introduce Na₂O and CaO, respectively. Ammonium dihydrogen orthophosphate [NH₄H₂PO₄] was responsible to introduce P₂O₅. Carbonates of potassium and magnesium, which are the raw materials for, K₂O and MgO respectively. The B₂O₃ is already present and was added to create Bioactive Glass (BG). Flow chart for melting of glass samples is represented in Figure 1 various glass samples



Figure 1. Flow chart for melting of glass samples.

1393 (G-1), G-2, G-3, G-4 and G-5 is depicted in Figure 2. Analytical grade chemicals made up every component of the batch, which was used without further purification. A list of Bioactive Glass (BG) compositions is provided in Table 1. A mortar and pestle were used to mix the weighed portions thoroughly. The mortar and pestle were professionally rinsed and desiccated moisture thoroughly before utilizing. materials for the batch were well mixed before being kept in crucibles made of alumina and heated in a furnace running by electricity. The temperature of the furnace was set to 1400 C by controlling the electricity supply, and after it reached that temperature, a constant condition was maintained for an additional 3 hours. When the melting process of the prepared bioactive was completed the liquid form of glass samples was poured into molds and in this condition, these samples were put into a muffle furnace temperature which can be controlled and maintained up to 500°C for the process of annealing. After an hour, the cooling process of the muffle furnace was started at room temperature In the process of melting of composition, some internal stresses generate and these stresses can be detached with help of annealing

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	SIO2	NajO	CaO	P ₂ O ₈	MgO	K <u></u> O	₿ Q;
G1	53	6	20	4	5	12	0
G2	3975	6	20	4	5	12	1325
G3	265	6	20	4	5	12	265
G4	1325	6	20	4	5	12	39.75
G5	0	6	20	4	5	12	53

 Table 1. The compositions of bioactive glasses.



Figure 2. Glass Sample 1393 (G-1), G-2, G-3, G-4 and G-5.

from the bioactive glass. Since those bioactive glasses had not followed the methods of annealing, therefore sudden change in temperature, often known as a thermal shock, or a mechanical shock might cause them to break. The heating process of the glass continues until it is soft enough to allow the tensions to relax but is still too rigid to deform.

2.2 Preparation of Simulated Body Fluid (SBF)

Kokubo and his colleagues developed a biotic simulated body fluid that has concentrations of ions that are released from inorganic materials. this fluid is well known by the name SBF and is responsible for the in vitro testing of bioactive glass. In the process of in vitro testing¹³, the presence of SBF generates a layer of apatite over the surface of bioactive glass. When there is a need of coating an apatite layer on the surface of any material, SBF can play a tremendous role, Table 2.

2.3 Powder X-ray Diffraction Analysis

There are various types of processes to determine the crystalline one of them is known as the XRD. In this way, glass has been converted in form of fine powder (70 μ m 80 μ m) with the help of grinding. The fine powder of glass is inspected by the process of X-ray Diffraction (XRD). When the process of measurement starts, the size of the step and speed of the step were set to 0.00033° and 0.016°

per second respectively meanwhile. The parameters for the step size and speed were 0.51° per minute, respectively. International Center for Diffraction JCPDS Data Cards was used as a source.

2.4 *In vitro* Bioactivity Study of Bioactive Glass

While in vitro test, samples of bioactive glass got ready for examination on the basis of their bioactivity. First of all 10 ml of SBF and 1g of samples were assorted and held on in the plastic container These plastic containers remained in an incubator at 37.50°C in a unique and similar environment for certain time periods of 2, 5, 7, 15, and 31 days. The samples are filtrated when they are drenched, washed with pure distilled water, and then start to dry for two hours in an electric air oven at 120°C. FTIR, XRD, and SEM techniques were used to determine the cause of the production of the layer of Hydroxy Carbonate Apatite (HCA) on the surface of the bioactive glass sample that comes in contact with SBF.

2.5 Structural Analysis of Bioactive Glasses

Using a technique FTIR (Fourier Transform Infrared Spectrometer), the functional groups of glass samples were investigated at average room temperature when the frequency range was 4000-400 cm⁻¹ (VARIAN scimitar 1000, USA). To create clear, homogenous discs, glassceramic powder of acceptable nature samples and KBr were assorted in a proportion of 1:100, respectively, and then the mixes were sent through an evocable die at a pressure of 10 MPa. In order to prevent moisture assault, the discs were immediately placed in an IR spectrometer to measure the absorption spectra. For 2, 5, 7, 15, and 31 days, the sample (one gram) was immersed in 10 ml of SBF solution with a pH value of 7.4 in a plastic container at 37.5°C. The samples were filtered after soaking and then dried for two hours at 120 °C in an oven. After that, FTIR analysis is performed.

Table 2. Ion content (mM/litre) of SBF and human blood plasma

Ion	\mathbf{Na}^{\dagger}	\mathbf{K}^{+}	\mathbf{Ca}^{2^+}	Mg^{2+}	HCO ₃	CÍ	HPO ²⁻	SO4 ²⁻
Simulated Body Fluid	142	5	2.5	1.5	4.2	148	1	0.5
Blood plasma	142	5	2.5	1.5	27	103	1	0.5

2.6 Mechanical Behavior

Microhardness tests of the bioactive glasses with 6mm x 6mm x 6mm dimensions being well polished and performed by a Digital hardness tester by using ASTM C730-98. The loading that is responsible for indentations was fluctuating from 30.00 MN to 2000.00 MN, at the rate of 1.00 mm/s. Microhardness (H) was evaluated using the formula (2) given below,

$$H = 1.854 (P/d^2)$$
(2)

In this formula, P represents the value of load that applied load on the sample, and the indication of diagonal (m) is represented by d (m).

The fine ground glass powder was pelletized into $25 \times 10 \times 10$ mm dimensions for a bending test using 3-point. The measurement was performed at 25°C using Tinius Olsen H10KL (USA) of 0.5 mm/min cross-head speed at a maximum loading of 10kN. Flexural strength (σ) was assessed with the help of ASTM C1674-11 as (3) follows

 $\sigma = (3PL)/(2bh^2)$

In the above formula, the value of load applied is denoted by P and the other parameters as length, breadth, and height are represented by L, b, and h respectively.

(3)

3.0 Result and Discussion

3.1 X-Ray Analysis of 1393 (G-1) and Replacement of Silica by Boron Trioxide Glass

The patterns of the XRD for the bioactive glass samples G1, G2, G3, G4 and G5 are shown in Table 1. The findings are in stalwart agreement with the idea that the nature of glass is an amorphous substance; as a result, Figure 3 lacks any peaks, indicating the lack of any crystalline phase. Replacement of silica in the place of boron trioxide in the glass network has been intensified by the hump for 2θ varying 35 to 25 that depict the dissolving nature of boron oxide in the matrix of glass²⁵.

3.2 FTIR 1393 (G-1) and Replacement of Silica by Boron Trioxide Glass

Figure 4, shows (FTIR) absorbance spectra of bioactive glasses before immersion into the SBF. The trend was for G1 and G2 to exhibit almost the same peak, at



Figure 3. X-Ray diffraction of bioglass samples before SBF.

wave numbers 1337 cm⁻¹ and cm⁻¹, respectively. There are different peaks at 1030 cm⁻¹ and 944 cm⁻¹ that are represented by samples G1 and G2. With the help of the infrared spectrum band table, it can be concluded that indications of these peaks ensured the bond of -O-Si- and bond of -Si-P- bond¹⁷⁻²¹. The other three glasses are exhibiting peaks in the range 1561, 1555, and 1557 cm⁻¹, 1337 cm⁻¹, and 944, 942, and 946 cm⁻¹. The 1337 cm⁻¹ is the wave number denoted to the bond of P = O²²⁻²³. The 1556 cm⁻¹ is another wave number that indicates the bond -Si-P-²⁴⁻²⁵. The peaks of the spectrum by FTIR inspection of G2, G3, G4, and G5 samples have the same behavior as G1 with a slight change in the intensities of the peaks as shown in Figure 4.

3.3 Flexural Strength and Microhardness

When the Ions of boron (ionic radius ~ 1.3 Å) are replaced by Si²⁺ ions there is no major change in glass structure but the result of this replacement could show an increment in the density of the glass¹¹⁻¹⁵. when the mechanical evaluation



Figure 4. FTIR of bioglass samples after 13 days in SBF.



Figure 5. Flexural Strength and Micro hardness of samples G1, G2, G3, G4 and G5 respectively.

of base glass is performed some crucial results have been found in this analysis and are micro hardness and flexural

strength of base glass (Figure 5) is 6.92 GPa and 56.87 MPa respectively while the samples of bioglass after substitution represent enhancement in microhardness and flexural strength in (G1, G2, G3, G4 andG5) and flexural strength in MPa of the samples increases when the percentage of boron trioxide enhanced. As a result of the glass powder's compact molecular structure, adding boron ions boosted the micro hardness and flexural strength of the material.

4.0 Conclusion

The XRD examination showed the non-crystalline of the glass, FTIR absorbance spectra shows the arrangement of the HCA layer on a superficial level G-1, G-2, G-3, G-4, and G-5 bioactive glasses after dipping into SBF. In this way, it very well may be closed from the exploratory work that all the substitution of silica by boron trioxide glass bioactive glass have shown superior properties. Among every one of the examples, the G-4 glass is the best one as it has shown the higher form of the HCA layer. It tends to be seen from the FTIR graph of G-4 that every one of the bonds is showing noticeable HCA layer formation. It also shows that mechanical behavior also enhances considerably by substituting B_2O_3 . The pre-arranged bioactive glasses can be utilized with respect to bone tissue designing applications.

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6.0 References

- Hench LL. Bio-ceramics. J Am Ceram Soc. 1998; 74(7):1487-510. https://doi.org/10.1111/j.1151-2916. 1991.tb07132.x
- Gerhardt LC, Boccaccini AR. Bioactive Glass and Glass-Ceramic Scaffolds for Bone Tissue Engineering. Materials. 2010; 3:3867-910. https://doi.org/10.3390/ ma3073867 PMid:28883315 PMCid:PMC5445790

- 3. Ylanen HO. Bioactive glasses materials properties and applications. Biomaterials. 2011; 6:1-288.
- Fredholm YC, Karpukhina N, Law RV, Hill RG. Strontium-containing bioactive glasses: Glass structure and physical properties. J Non-Cryst Solids. 2010; 356:2546-51. https://doi.org/10.1016/j.jnoncrysol.2010.06.078
- Balamurugan A, Rebelo AH, Lemos AF, Rocha JH, Ventura JM, Ferreira JM. Dent Mater. 2008; 24:1374-1380. https://doi.org/10.1016/j.dental.2008.02.017 PMid:18417203
- Oki A, Parveen B, Hossain S, Adeniji S, Donahue H. Preparation and in vitro bioactivity of zinc containing sol-gel-derived bioglass materials. J Biomed Mater Res A. 2004; 69:216-21. https://doi.org/10.1002/jbm.a.20070 PMid:15057994
- 7. Saboori A, Sheikhi M, Moztarzadeh F, Rabiee M, Hesaraki S, Tahriri M. Sol-gel preparation, characterisation and in vitro bioactivity of Mg containing bioactive glass. Adv Appl Ceram. 2009; 108:55-161. https://doi.org/10.1179/174367608X324054
- 8. Du W, Kuraoka K, Akai T, Yazawa T. Study of Al_2O_3 effect on structural change and phase separation in $Na_2O-B_2O_3$ -SiO₂ glass by NMR. J Mater Sci. 2000; 35:4865-71. https://doi.org/10.1023/A:1004845817600 https://doi.org/10.1023/A:1004706828073 https://doi.org/10.1023/A:1004853603298
- Yun YH, Bray PJ. Nuclear magnetic resonance studies of the glasses in the system Na₂O-B₂O₃-SiO₂. J Non Cryst Solids. 1978. Available from: https://linkinghub.elsevier.com/retrieve/pii/0022309378900200. https://doi. org/10.1016/0022-3093(78)90020-0
- 10. Dell WJ, Bray PJ, Xiao SZ. 11B NMR studies and structural modeling of Na₂O-B₂O₃-SiO₂ glasses of high soda content. J Non Cryst Solids. 1983. Available from: https://linkinghub.elsevier.com/retrieve/pii/0022309383900972. https://doi.org/10.1016/0022-3093(83)90097-2
- Manara D, Grandjean A, Neuville DR. Structure of borosilicate glasses and melts: A revision of the Yun, Bray and Dell model. J Non Cryst Solids. 2009. Available from: https://linkinghub.elsevier.com/retrieve/pii/ S0022309309005845. https://doi.org/10.1016/j.jnoncrysol.2009.08.033
- 12. Kokubo T, Takadama H. How useful is SBF in predicting in vivo bone bioactivity. Biomaterials. 2006; 27:2907-15. https://doi.org/10.1016/j.biomaterials.2006.01.017 PMid:16448693

- Ducheyne P, Hench LL, Kagan I, Martens A, Bursens A, Mulier JC. Effect of hydroxyapatite impregnations on skeletal bonding of porous coated implants. J Biomed Mater Res. 1980; 14:225-37. https://doi.org/10.1002/ jbm.820140305 PMid:7364787
- Koutsopoulos S. Synthesis and characterization of hydroxyapatite crystals: A review study on the analytical methods. J Biomed Mater Res. 2002; 62(4):600–12. https://doi.org/10.1002/jbm.10280 PMid:12221709
- 15. Ali A, Singh BN, Yadav S, Ershad M, Singh SK, Mallick SP, Pyare R. CuO assisted borate 1393B3 glass scaffold with enhanced mechanical performance and cytocompatibility: An In vitro study. J Mech Behav Biomed Mater. 2021; 114:104231. https://doi.org/10.1016/j.jmbbm.2020.104231 PMid:33276214
- Ershad M, Vyas VK, Prasad S, Ali A, Pyare R. Synthesis and characterization of cerium- and lanthanumcontaining bioactive glass. Key Eng Mater. 2017; 751:617-28. https://doi.org/10.4028/www.scientific.net/ KEM.751.617
- Gabelica-Robert M, Tarte P. Infrared spectrum of crystalline and glassy pyrophosphates: preservation of the pyrophosphate group in the glassy structure. J Mol Struct. 1982; 79:251. https://doi.org/10.1016/0022-2860(82)85061-8
- Salim MA, Khattak GD, Sakhawat Hussain MJ. X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and electrical conductivity studies of copper phosphate glasses. Non-Cryst. 1995; 185:101. https://doi.org/10.1016/0022-3093(94)00683-0
- Chahine A, Et-tabirou M, Pascal JL. FTIR and Raman spectra of the Na₂O-CuO-Bi₂O₃-P₂O₅ glasses. Materials Letters. 2004; 58:2776-80. https://doi.org/10.1016/j.matlet.2004.04.010
- Rehman I, Karsh M, Hench LL, Bonfield W. Analysis of apatite layers on glass-ceramic particulate using FTIR and FT-Raman spectroscopy. J Biomed Mater Res. 2000; 50(2):97-100. https://doi.org/10.1002/(SICI)1097-4636(200005)50:2<97::AID-JBM1>3.0.CO;2-7
- 21. Vyas VK, Kumar AS, Ali A, Prasad S, Srivastava P, Mallick SP, Ershad M, Singh SP, Pyare R. Assessment of nickel oxide-substituted bioactive glass-ceramic on in vitro bioactivity and mechanical properties. Bol Soc Esp Ceram Vidrio. 2016; 55(6):228-38. https://doi. org/10.1016/j.bsecv.2016.09.005
- 22. Ali A, Ershad M, Vyas VK, Hira SK, Manna PP, Singh BN, Yadav S, Srivastava P, Singh SP, Pyare R. Studies on the effect of CuO addition on mechanical properties

and in vitro cytocompatibility in 1393 bioactive glass scaffold. Materials Science and Engineering: C. 2018; 93:341-55. https://doi.org/10.1016/j.msec.2018.08.003 PMid:30274066

- 23. Ershad M, Ali A, Mehta NS, Singh RK, Singh SK, Pyare R. Mechanical and biological response of (CeO²⁺La₂O₃)-substituted 45S5 bioactive glasses for biomedical application. J Aust Ceram Soc. 2020; 56(4):1243-52. https://doi.org/10.1007/s41779-020-00471-3
- Ershad M, Vyas VK, Prasad S, Ali A, Pyare R. Effect of Sm₂O₃ substitution on mechanical and biological properties of 45S5 bioactive glass. J Aust Ceram Soc. 2018; 54(4):621-30. https://doi.org/10.1007/s41779-018-0190-7
- 25. Ali A, Ershad M, Hira S, Pyare R. Mechanochemical and in vitro cytocompatibility evaluation of zirconiamodified silver-substituted 1393 bioactive glasses. Bol Soc Esp Ceram Vidrio. 2022; 61(1):64-75. https://doi. org/10.1016/j.bsecv.2020.07.002