International Journal of Engineering Research and Development
e-ISSN: 2278-067X, p-ISSN: 2278-800X, www.ijerd.com
Volume 12, Issue 10 (October 2016), PP.21-28

Physico-Mechanical Properties of TiO_2 Doped 45S5 Bioactive Glasses and Glass –Ceramics

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Abstract: TiO_2 doped 45S5 bioactive - glasses were prepared. Bioactive Glass - ceramics were obtained through controlled crystallization of bioactive glasses. Nucleation and crystal Growth temp. Were determined by the parameters obtained from differential thermal analysis (DTA) of bioactive - glasses. The crystalline phases which are formed in bioactive glass - ceramics were recognized by using X - ray diffraction (XRD) study. The density of bioactive glass and glass - ceramic samples was obtained by Archimedes principle using distilled water as buoyant. The Mechanical properties like compressive strength and flexural strength of TiO2 doped bioactive glasses and glass – ceramics were measured. Experimental results show that a increase in glass nucleation and crystallization temperature of bioactive - glass by doping of TiO_2 in it and the formation of crystalline phases of sodium calcium silicate and calcium titanium silicate in bioactive glass - ceramics. The density of bio glass and glass ceramics are increase with increases the TiO_2 amount in weight %**.** The Mechanical properties like compressive strength and flexural strength of bioactive glass - ceramics are found higher than their respective bioactive glasses and also it increases by doping TiO2.

Keywords: Bio ceramics, Bioactive Glasses, Bioactive Glass - ceramics, Physical Properties, Mechanical Properties

I INTRODUCTION

Various types of bioactive materials have been developed over some previous years. Among them the main material is bio material. The definitions of biomaterial were given as "Material that is used to replace or repair a body tissue and is constantly or intermittently in contact with body fluids known as a biomaterial" (Park 1984). Another definition of a biomaterial, it is a non- toxic material that can be used to construct artificial organs, remedy devices and to replace tissues. Bio material are produced a different kind of form, phases and functions in reconstruction in the body. The main bioactive materials used in medical field are: bioactive glasses in the SiO_2 - Na_2O - CaO - P_2O_5 system [1], bioactive glass - ceramic A - W containing crystalline oxyfluoroapatite [Ca10(PO4)6(O, F)2] and β - wollastonite [CaO.SiO2] in a MgO - CaO - SiO2 glassy matrix [2], hydroxyapatite (HA) [Ca10(PO4)6(OH)2] and β – tri calcium phosphate (TCP) [Ca3(PO4)2] . A bioactive material is considered as interface that results in the formation of a bond between tissues and the materials [3]. The most widely used in medical field bioactive material is 45S5 bioactive glass [composition in wt. %: 45 SiO_2 - 24.5 Na_2O - 24.5 CaO - 6 P_2O_5], where SiO_2 denotes the network former which in 45% by weight [4]. 45S5 bioactive glass was discovered by Hench in 1969 at Florida University. It is a biocompatible and shows high bioactivity nature which is in fact clinically used for middle ear prostheses and as end osseous edge implants [5]. A major drawback of 45S5 bioactive glass is linked to its time-consuming degradation rate. In addition, the Mechanical property of 45S5 bioactive glass is poor for significant load - bearing applications [6]. Previous studies [7] have shown that the substitution of 5 - 15% B_2O_3 for SiO_2 or 12.5% CaF_2 for CaO or Na_2O in 45S5 bioactive glass has little effect on the ability of its inter- facial bond formation between tissue and implant. In order to increase durability of phosphate glasses, attempts have been made to investigate the effect of doping of metal ions on the phosphate based glass network. The addition of oxides such as CoO, ZnO, NiO, CuO and Fe_2O_3 to phosphate based glasses have little effect on their mechanical, physical, chemical and bioactive properties[8]. Addition of B_2O_3, MgO, CaF_2 or TiO_2 generally leads to glass–ceramic materials which also show bioactivity in nature [9]. Chemical stability of glasses depends on its size of ion and charge nature of the doping ions. Tio2, normally known to have good hemocompatiblity and non-toxicity to experimental in living tissue, which are very useful in clinical fields. Many literatures are available on phosphate-based bio glasses and glass - ceramics with different contents of TiO_2 in order to investigate the physical, chemical, mechanical and biological properties of materials [10-14].

Application of glass–ceramics in the field medical is limited due to their inherent mechanical properties such as brittleness, low tensile strength, micro hardness, flexural strength and difficulty in coating onto other materials [15].

II REVIEW OF LITERATURE

Any natural or synthetic material that is implanted in living body known as biomaterial. According to Williams a "biomaterial is non- toxic material of natural or manmade origin, which is projected to interface with a biological system to treat, expand or replace any tissue, organ, or function of the body and that evokes a minimal biological response" (Ratner et al.1996).There are four types Bio Ceramic tissue Attachment. it is thought that interactions between body and implants could cause only undesirable reactions, such as tissue pain, damage, and finally death. This is occurred if a toxic material is plant in contact with a living tissue, it will die. Due to this reason, the guiding principle used in development of biomaterial which should be chemically inert in nature as possible [16].

III EXPERIMENTAL PROCEDURE

A. Composition of tio2 doped 45s5 bioactive glass (bg) samples:

Table 1: Composition of TiO_2 Doped 45S5 bio glass (BG) samples

Sample	Na_2O (wt%)	SiO_2 (wt%)	CaO (wt%)	P_2O_5 (wt%)	TiO_2 (wt%)
BG 0.0	24.5	45	24.5	6	-
BG 0.5	24.0	45	24.5	6	0.5
BG 1.0	23.5	45	24.5	6	1.0
BG 1.5	23.0	45	24.5	6	1.5
BG 2.0	22.5	45	24.5	6	2.0
BG 3.0	21.5	45	24.5	6	3.0

The composition of 45S5 bio glasses is 45% SiO_2, 24.5% Na_2O, 24.5% CaO, 6% P_2O_5 (expressed in weight %). In the base composition of 45S5, Na_2O percentage is replaced by TiO_2 Percentage in amount of 0.5%, 1.0%, 1.5%, 2.0%, and 3.0%. Which are shown in the above table, and there is no changes in other composition percentage like SiO_2, CaO, P_2O_5. There are six samples which are denoted by BG 0.0, BG 0.5, BG 1.0, BG 2.0, and BG 3.0 shown in table 1.

B. Preparation method of TiO_2 doped 45S5 bioactive glass (BG) samples:

For the preparation of the compositions of bio glass, AR grade Quartz, $CaCO_3$, Na_2CO_3, $NH_4H_2PO_4$, and TiO_2 were taken as batch chemicals in the calculated proportions for each 100 gms. Further batch materials were mixed in mortar with pestle for about half an hour to get a hold a homogeneous mixture. The mixed batch was then transferred into an alumina crucible. The crucible was further placed into the Globar rod furnace for melting at room temperature. The bio glass batches were melted in the furnace at 1400 ^{0}C and hold for three hours. Further the melted glass was taken out from the furnace with the help of the forcipes and poured on the aluminum sheet in a preheated stainless steel rectangular mould and placed it in the annealing furnace at 500 ^{0}C to room temp.. The annealed bio glass samples are then cut down into the desired dimensions with the help of diamond saw cutter and then grind and polished the samples for characterization purpose.

C. preparation method of TiO_2 doped 45S5 bioactive glass ceramics (GC)samples:

To make the bioactive glass ceramics, the bioactive glass samples were heated in muffle furnace in two step at the deduced temperatures and times as shown in table. These temperatures were obtained from differential thermal analysis (DTA) of bioactive glass samples. Every sample was first heated slowly for the nucleation and holds it for 6 hours. Then it was further heated to reach another temperature for the crystal growth and hold it for 3 hours, the sample was left for cooling from inside temperature to room temperature at a rate of 20 °c/h. The heat treatment schedule for the TiO_2 doped 45S5 bioactive glasses were given with the help of DTA plots of BG0.5, BG1.5, BG3.0 samples and a research paper [17].

Table 2: The heat treatment schedule for the TiO2 doped 45S5 bioactive glasses

Sample	Nucleation Temp.(Tg)	Growth Temp. (Tc)
	Temp.° c	Temp.° c
BG 0.0	540	730
BG 0.5	550	770
BG 1.0	572	775
BG 1.5	600	840
BG 2.0	620	845
BG 3.0	630	850

IV. MEASUREMENT AND CHARACTERIZATION

A. Physical analysis:

Differential thermal analysis (DTA):

Differential thermal analysis (DTA) is mostly used for thermal analysis method. In DTA, the temperature of a sample is compared with an inert reference material during a programmed change of temperature. The temperature should be the same until thermal event occurs like melting, decomposition or change in the crystal structure. In an endothermic event takes place in the sample, the temperature of the sample will decrease behind that of the reference and a minimum will be observed on the plot. On the contrary, if an exothermic event takes place, then the temperature of the sample wills increases that of the reference and a maximum will be observed on the plot. The area under the endothermic is related to the enthalpy of the thermal event, ΔH. For many problems, it is advantageous to use both DTA and TG, because the DTA events can then be divide into those which do or do not involve mass change. DTA/TGA analysis of ash has been done by up to 1000 0C.

(a) X-ray diffraction (XRD):

X-ray diffraction (XRD) is a multipurpose, non destructive technique which is used to know crystal Structure of materials. The basic geometry of an X-ray diffractometer involves a source of monochromatic radiation and an X-ray detector situated on the circumference of a graduated circle centered on the powder sample.

(b) Density measurement:

The density of bio glass and glass - ceramic samples was calculated by Archimedes principle using distilled water as buoyant. The weight measurements of all samples have been made using a digital balance having an accuracy of ± 0.0001 g. It is denoted by (ρ). The mathematical relation is used to calculate as given below formula.

$$\rho = \frac{w_a}{(w_a - w_b)} \rho_b$$

Where w_a is the weight of sample in air, w_b is the weight of sample in buoyant and ρ_b is the density of buoyant.

B. Mechanical properties measurement:

(a) Compressive strength measurement:

Compressive strength is the capacity of a material or structure to withstand loads which are apply to reduce size. It can be measured by ratio of applied force to the area. Some material sustained load at their compressive strength limit. Compressive strength is often measured on a universal testing machine (UTM). Compressive Strength is denoted by σ of sample is calculated using the formula as given below:

$$\sigma = \frac{F}{A}$$

Where, F = Load applied (N)

A = Area (m^2)

(b) Flexural strength measurement:

Three-point flexural strength tests were measured for polished bioactive glass and glass – ceramic sample, using a universal testing machine (UTM). The load was applied gradually over a 20 mm span and at the mid - point of the 4 mm x 40 mm surface using a cross - head speed of 0.5 mm/min. Flexural Strength is denoted by σ_f of sample is calculated using the formula as given below:

$$\sigma_f = \frac{3wL}{2bh^2}$$

Where w is the load at which specimen being fractured, L is the length of specimen over which the load is applied, b is the width of specimen, and h is the height of specimen.

V. RESULTS AND DISCUSSION

A. Physical Analysis:

(a) Differential thermal analysis (DTA) plot:

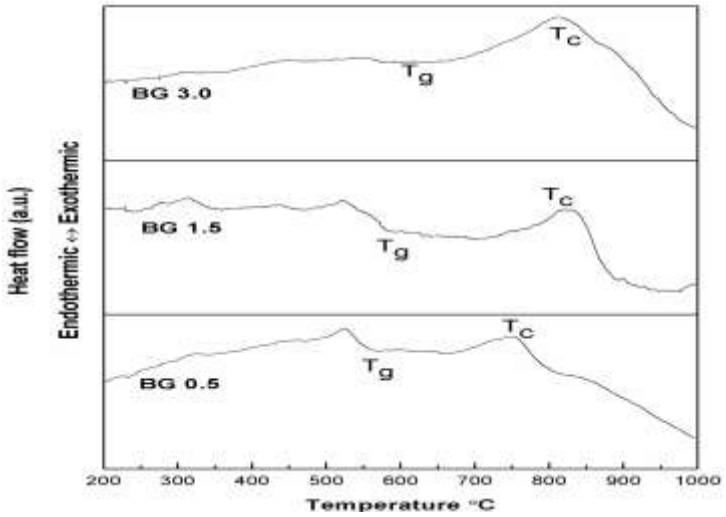

Figure1: Differential thermal analysis (DTA) plot of TiO2 doped 45S5 bioactive glasses samples
Tg - Nucleation Temperature, **Tc** - Crystallization Temperature

VI. Discussion

The differential thermal analysis (DTA) curves of bioactive glasses show the glass transition temperature (endothermic peak) in the range of 540-630 ^{0}C and crystallization temperature (exothermic peak) in the range of 730-850 ^{0}C. The substitution of Na_2O with TiO_2 increases the glass transition temp. (Tg) and crystallization temperature (Tc) with increases the TiO_2 amount from 0.5 to 3.0% as shown in above figure 1.

(c) XRD of bioactive glass (BG) samples:

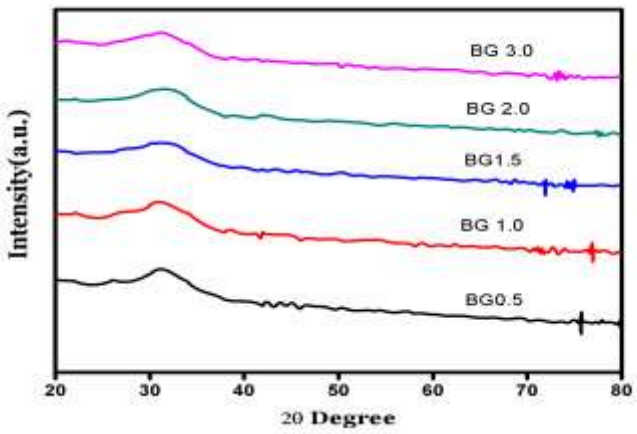

Figure 2: XRD of bioactive glass samples

Discussion: All prepared bioactive glass samples show amorphous in nature by XRD experiment of TiO_2 doped 45S5 bioactive glass samples because there was no peak found in XRD pattern, this shows our melting was homogeneous as shown in above figure 2.

(d) XRD of glass- ceramic (GC) samples:

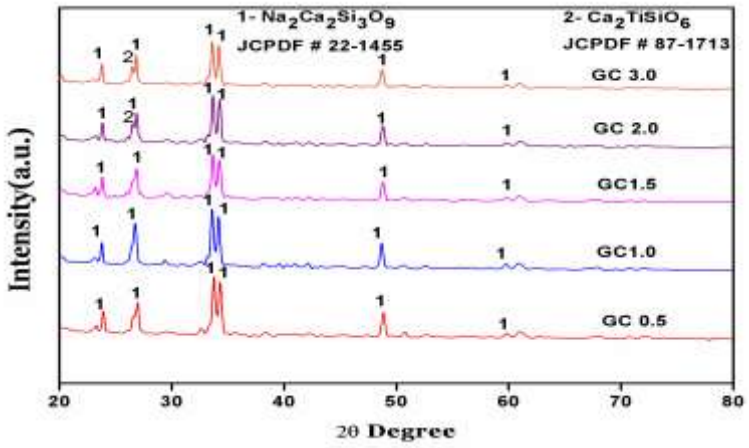

Figure 3: XRD of bioactive glass - ceramics samples

VII. Discussion

The XRD patterns of all TiO_2 doped bioactive glass – ceramics samples show the presence of crystalline phases. The XRD result of glass – ceramic samples shows the sodium calcium silicate ($Na_2Ca_2Si_3O_9$) JCPDF # 22 - 1455 as the main Crystalline phase, by increase TiO2 amount a new phase calcium titanium silicate (Ca_2TiSiO_6) JCPDF # 87 - 1713 is found in samples GC 2.0 and GC 3.0 as shown in above figure 3.

(e) Density measurement:

Table 3: Density of bio glass samples in (gm/cc) and Density of glass- ceramics samples in (gm/cc)

Sample	Density in (gm/cc)	Sample	Density in (gm/cc)
BG 0.0	2.69	GC 0.0	2.72
BG 0.5	2.71	GC 0.5	2.74
BG 1.0	2.72	GC 1.0	2.75
BG 1.5	2.74	GC 1.5	2.78
BG 2.0	2.77	GC 2.0	2.80
BG 3.0	2.78	GC 3.0	2.83

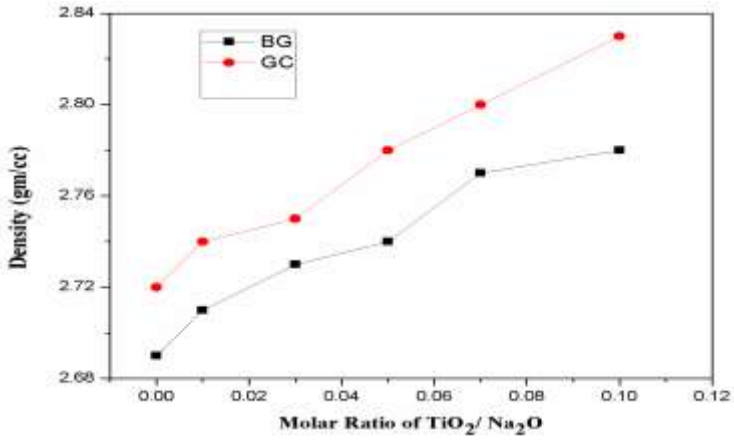

Figure 4: variation of density of bio glass and glass ceramics

Discussion

Density of bio glass and glass ceramics samples are increases with increase the molar ratio of TiO_2 / Na_2O. Density of glass ceramic samples is more as compared to bio glass due crystal phase formation. The density of bio glass is 2.69 gm/cc and density of TiO_2 is 4.23 gm/cc. Since TiO_2 is used as a doping agent which replaces Na_2O amount. Since TiO_2 has more density as compared to bio glass so its substitution increases the density of bio glass. Since bio glass is amorphous in nature, after heat treatment it transformed from amorphous phase to crystalline, due to this density of glass ceramic samples are more as compared to bio glass. In the figure 4: the density of bio glass and glass ceramics are increase with increases the TiO_2 amount in weight %.

(B) Mechanical Properties Measurement:

(a) Flexural strength of bioactive glasses and glass- ceramics:

Table 4: Flexural Strength of bioactive glass (MPa) and Flexural Strength of glass ceramics (MPa)

Sample	**Flexural Strength (MPa)**	**Sample**	**Flexural Strength (MPa)**
BG 0.0	60.68	GC 0.0	108.19
BG 0.5	85.22	GC 0.5	113.37
BG 1.0	102.65	GC 1.0	122.46
BG 1.5	109.35	GC 1.5	130.38
BG 2.0	116.78	GC 2.0	150.46
BG 3.0	130.34	GC 3.0	175.32

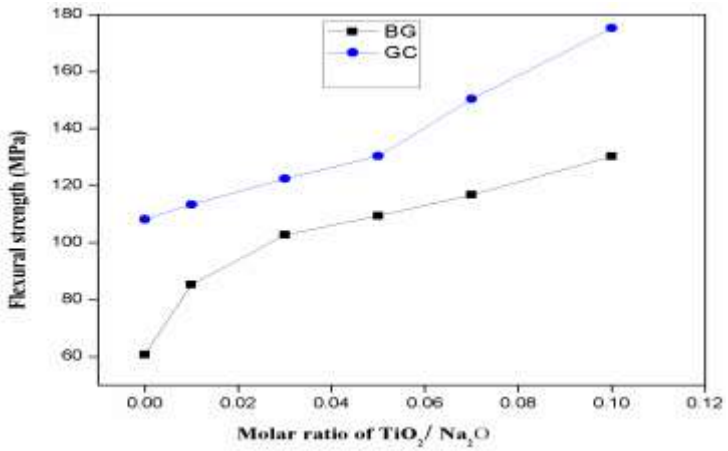

Figure 5: variation of flexural strength of bioactive glasses and glass ceramics

Discussion

Flexural strength of bio glass samples and glass ceramics samples both are increases with increase the molar ratio of TiO_2 / Na_2O. Flexural strength of glass ceramic samples is more as compared to bio glass due crystal phase formation as shown in above figure 5.

(b) Compressive strength of bioactive glasses (BG) and glass - ceramics (GC) (MPa):

Table 5: Compressive Strength of bioactive glass samples (MPa) and glass ceramics samples (MPa)

Sample	Compressive Strength (MPa)	Sample	Compressive Strength (MPa)
BG 0.0	115	GC 0.0	129
BG 0.5	119	GC 0.5	136
BG 1.0	127	GC 1.0	145
BG 1.5	139	GC 1.5	167
BG 2.0	147	GC 2.0	189

BG 3.0	161	GC 3.0	205

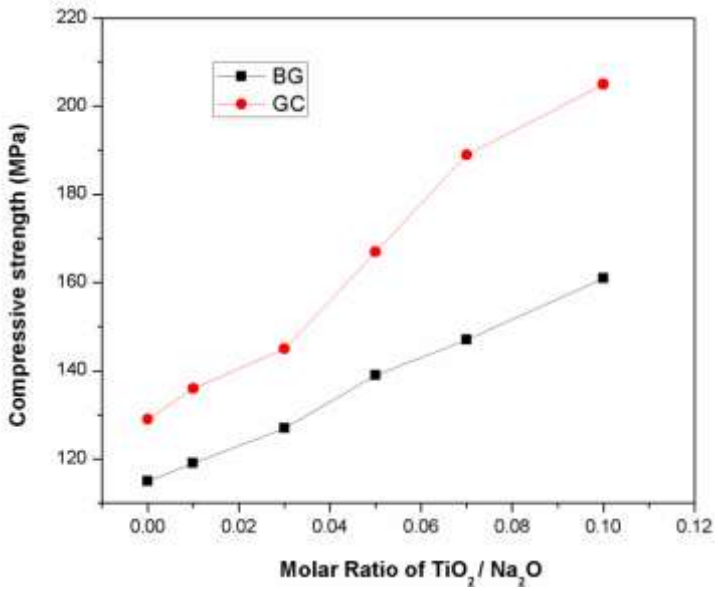

Figure 6: variation of compressive strength of bio glasses and glass ceramics

Discussion

Compressive strength of bio glass samples and glass ceramics samples both are increases with increase the molar ratio of TiO_2 / Na_2O. Compressive strength of glass ceramic samples are more as compared to bio glass due to loss of porosity as shown in above figure 6.

VIII. CONCLUSIONS

- All the bio glass samples could be successfully prepared for characterization purpose by melt route.
- On increasing the substitution of TiO_2 in place of Na_2O, the nucleation and crystallization temperature increases with increasing amount of TiO_2.
- Density of bio glass and glass- ceramic samples increases with increase in amount of TiO_2. Density of glass ceramics more than bio glass due to crystal formation.
- All prepared bio glass samples were found amorphous by XRD experiments.
- The XRD result of glass ceramic show the sodium calcium silicate ($Na_2Ca_2Si_3O_9$) as the main phase.
- By increases TiO_2 amount, new phase calcium titanium silicate (Ca_2TiSiO_6) are found in sample GC 2.0 and GC 3.0.
- Flexural strength and Compressive strength of bio glass samples and glass ceramics samples were increases when amount of TiO_2 are increases. Flexural strength and Compressive strength of glass ceramic samples are more as compared to bio glass due to less porosity.

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