

## **CHAPTER-3**

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**Fabrication and analysis of the  
effect of doping  $\text{TiO}_2$  in 1393  
bioactive glass**

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### 3.1 Introduction

Bioactive glasses are of importance for biomedical applications due to their ability to chemically bond to bone and stimulate new bone growth [Liu et al., 1994], excellent mechanical stability [Hench et al., 1991] and making free from disease [Buck et al., 1989 and Hench et al., 1993]. Under physiological conditions, bioactive glasses liquefy in a controlled manner releasing calcium and phosphorous ions into solution [Hench et al., 2006]. Ca and P form a non-crystalline calcium phosphate layer (ACP) which then crystallizes to form hydroxyapatite (HA) / Hydroxyl-carbonate apatite (HCA): the naturally occurring mineral present in both teeth and bones [L.L. Hench and O. Andersson, 1993 and Splinter et al., 1971]. Recent developments in tissue engineering in the field of orthopedic implants look forward to develop the regeneration capabilities of the host tissues using most recent designing methods for research of implants to match the structure of the host tissues to accelerate the rejuvenation of the dead tissues [K. Franks and I. Abrahams, 2001; V. Patricia and M.P. Marinade, 2004; Oana Bretcanu et al., 2009; Fathi and Hanifi, 2007; Kansal and Goel, 2011]. This requires the preparation of implants which are similar to that of the host tissue structure both in terms of the arrangement as well as mechanical and biological properties [Kokubo and Kim, 2003; Shim and Wechsler, 1996; Watts and Hill, 2010; Rezwan and Blaker, 2006; Austin and Smith, 2013]. In reference to the more than requirements, bioactive glasses have shown capable prospects. Due to their class bioactivity showing both osteoconduction and osteoproduction, have become the material of major interest. Since the revolutionizing paper by Hench on bioactive glass in the 70s, the composition has been optimized several times for better results than the last one [Kaur and Sharma, 2012; Leenakul and Kantha, 2013; Vogel et al., 1969; Kokubo and Takadama, 2006; Sooksaen and Suttiruengwong, 2008]. Glasses are

composed of network forming, modifying, and intermediate oxides. They present a non-crystalline character reflecting structural disarray. Metal elements introduced in the glass matrix may involve specific changes in thermal behavior [Bretcanu et al., 2009]. In the glassy form, if there are not enough alkaline ions, the intermediate element will be a network modifier by creating two oxygen bridges [Peitl Filho et al., 1996 and Zanotto et al., 2000]. Conversely, if there are enough alkaline ions, the intermediate element will be a network former. Studies have shown the impact of titanium on the thermal properties [Clark et al., 1989 and Azooz et al., 2003]. Numerous researches about boron phosphate glasses have shown the effect of the addition of TiO<sub>2</sub> on their heat treatment characteristics. The results showed a non-linear change of glass transition temperature [Gayathri Devi et al., 2010]. In the present investigation, an attempt has been made to study the effect of titanium oxide doping in base 1393 bioactive glasses to find its bioactivity and mechanical behavior.

### **3.2 Material and methods**

#### **3.2.1 Selection of composition and preparation of the bioactive glasses**

The bioactive glass composition was formulated from 53SiO<sub>2</sub>-6Na<sub>2</sub>O-12K<sub>2</sub>O-5MgO-20CaO-4P<sub>2</sub>O<sub>5</sub> glass system. Proposed bioactive glasses containing chemical composition having wt% composition (53-X)SiO<sub>2</sub>-XTiO<sub>2</sub>-6Na<sub>2</sub>O-12K<sub>2</sub>O-5MgO-20CaO-4P<sub>2</sub>O<sub>5</sub> (where X=0-2wt) was prepared. In the present study, the CaO, Na<sub>2</sub>O, MgO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> concentration was kept constant, and SiO<sub>2</sub> was partially replaced with titanium oxide. The compositions of prepared bioactive glasses are given in Table-3.1. The bioactive base glass and titanium oxide doped glass were prepared by addition of titanium oxide (0-2 gram) in place of SiO<sub>2</sub> using the normal melting and annealing technique. Materials used include fine-grained quartz for silica. Lime and soda were introduced in the form of their respective anhydrous carbonates; potassium carbonate

for  $K_2O$ , anhydrous magnesium carbonate was used as the source of  $MgO$ .  $P_2O_5$  was added in the form of ammonium dihydrogen phosphate. We did not use  $P_2O_5$  directly due to hygroscopic in nature. The weighed batches were mixed thoroughly for 30 minutes and melted in 100 ml alumina crucibles to get the desired bioactive glass composition as given in Table-3.1. The melting was carried out in an electric furnace at  $1400\pm 5^\circ C$  for 3 hours in the air as furnace atmosphere and homogenized melts were poured on the preheated aluminum sheet. The prepared bioactive glass samples were directly transferred to a regulated muffle furnace at  $470^\circ C$  for annealing. After 2 hour of annealing, the muffle furnace was cooled to room temperature with a controlled rate of cooling at  $100^\circ C/h$ .

### 3.2.2 Characterization

The whole Characterization for titanium oxide doped bioactive glass have been discussed in chapter 2 like Preparation of SBF, powder X-ray diffraction (XRD) measurements, structural analysis of bioactive glass by FTIR spectrometry, In vitro bioactivity study of bioactive glass, mechanical behavior measurements, pH measurement, Surface morphology of bioactive glass sample by SEM and elastic properties of bioactive glasses.

Table 3.1- Composition of bioactive glass (wt %)

	<b>SiO<sub>2</sub></b>	<b>Na<sub>2</sub>O</b>	<b>CaO</b>	<b>P<sub>2</sub>O<sub>5</sub></b>	<b>TiO<sub>2</sub></b>	<b>K<sub>2</sub>O</b>	<b>MgO</b>
<b>1393</b>	53.00	6.00	20.00	4.00	0.00	12.00	5.00
<b>TiO<sub>2</sub>-1</b>	52.50	6.00	20.00	4.00	0.50	12.00	5.00
<b>TiO<sub>2</sub>-2</b>	52.00	6.00	20.00	4.00	1.00	12.00	5.00
<b>TiO<sub>2</sub>-3</b>	51.50	6.00	20.00	4.00	1.50	12.00	5.00
<b>TiO<sub>2</sub>-4</b>	51.00	6.00	20.00	4.00	2.00	12.00	5.00

### 3.3 Results and discussion

#### 3.3.1 Structural analysis of bioactive glasses

The X-Ray diffraction (X-RD) patterns for 1393 bioactive glass and titanium oxide doped 1393 bioactive glasses are shown in Figure:-3.1. The observed result indicates that the glasses have an amorphous structure, and there is no indication for the presence of crystalline phases. It was observed that with increase in concentration of titanium oxide in the composition, the broad hump at  $2\theta$  between  $25^\circ$  to  $35^\circ$  become more intense. This may be due to the  $Ti^{4+}$  expanding the silica network [Rajendran et al., 2010]

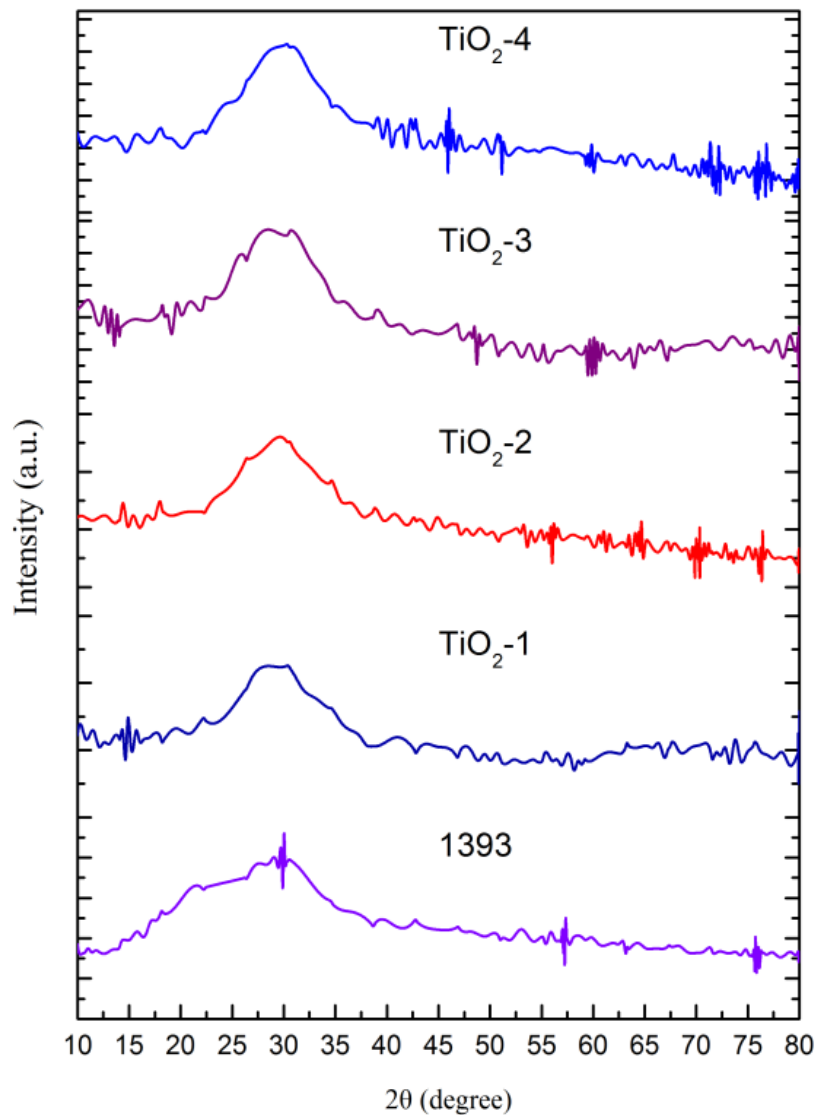


Figure 3.1- XRD of base and titanium dioxide doped bioactive glass

**Figure:-3.2** shows the FTIR Reflection spectra of the 1393 and titanium oxide doped bioactive glass before SBF treatment. All the bioactive glass samples are showing similar trend behavior, FTIR Reflection spectra bands of all the glasses confirm the main characteristic of silicate network and this may be due to the presence of SiO<sub>2</sub> as a major constituent.

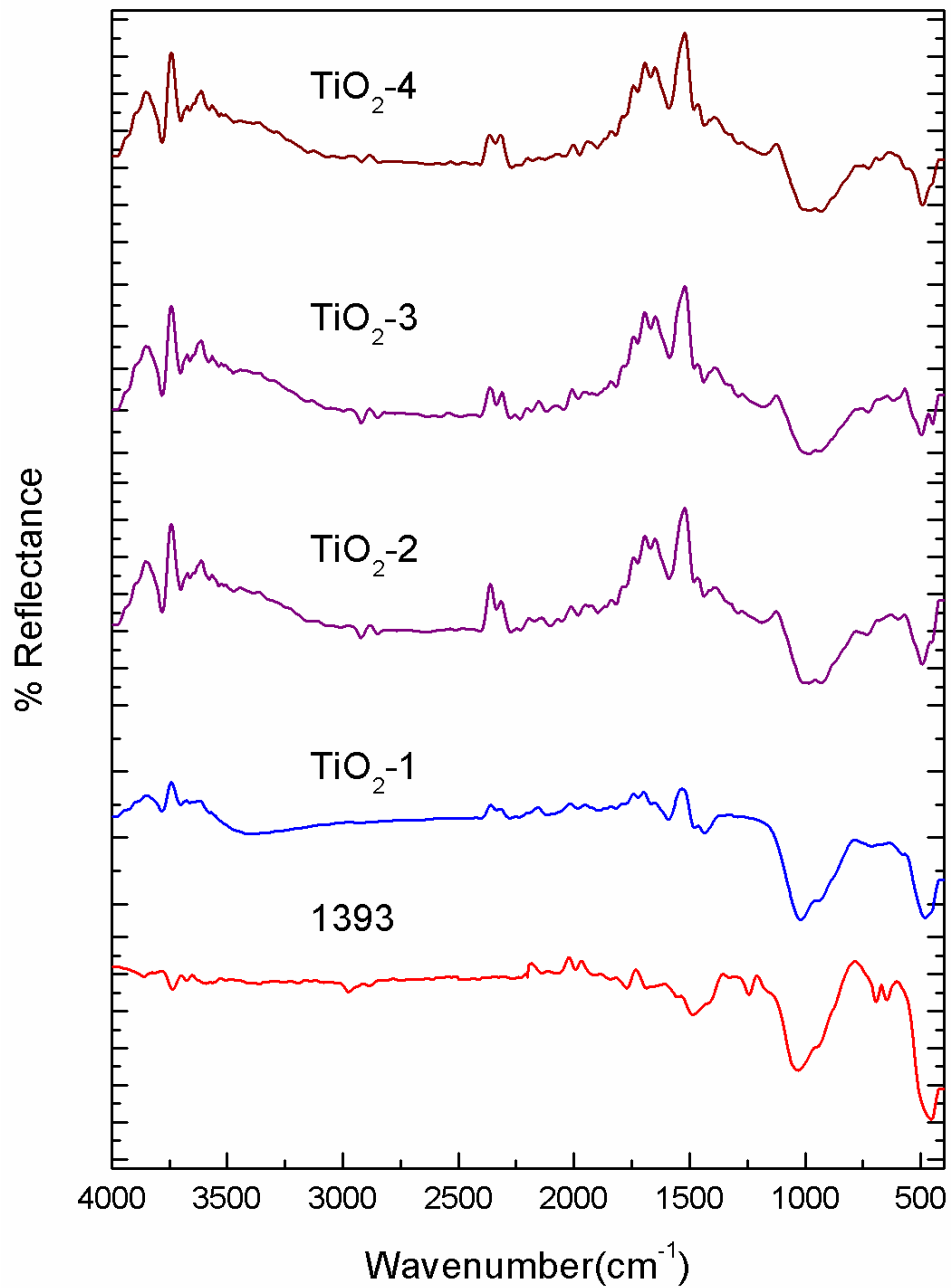


Figure 3.2- FTIR reflectance spectra of base and titanium dioxide doped bioactive glasses before immersion in SBF

Therefore, the bioactive glass (TiO<sub>2</sub>-1) shows the peaks at 470, 722, 1022, 1430 and 3775 cm<sup>-1</sup>. The resultant IR spectra at 470 cm<sup>-1</sup> associated with a Si–O–Si symmetric bending mode, the band at 722 cm<sup>-1</sup> corresponds with Si–O–Si symmetric stretch of non-bridging oxygen atoms between tetrahedral. It was observed that the intensity of the band recreated as the titanium oxide substitution in the 1393 bioactive glasses; therefore, the titanium oxide increases the non-bridging oxygen in the network. The major band at about 1022 cm<sup>-1</sup> can be attributed to Si-O-Si stretching. The small band at 1430 cm<sup>-1</sup> attributed to C–O vibration mode. It was noticed that the intensity of the IR peak increased as the concentration of titanium oxide increase, which is due to the breaking of the Si-O-Si network. The small, broadband centered at about 3775 cm<sup>-1</sup> can be assigned to the hydroxyl group (–OH) which may be due to the presence of adsorbed water molecules. Fig 3.2, depicts the infrared frequencies and related functional, structural groups in the bioactive glass [Nayak et al., 2010]. The bioactive glasses substituted with titanium oxide are not showing noticeable changes in the IR spectra bands.

### 3.3.2 pH behavior in SBF

The variation in pH values of simulated body fluid (SBF) after soaking of 1393 bioactive glasses for various time periods is shown in **Figure:- 3.3**. It was observed that the pH of all samples shows a similar trend of behavior [Marta Cerrutia et al., 2005]. The maximum pH values were recorded in three days of immersion. It is interesting to note that the Ti-doped bioactive glasses demonstrated a higher pH value after immersion in SBF which is due to the fast release of cations from the level surface compared with 1393 bioactive glass sample. It was observed that due to the addition of titanium oxide in bioactive base glass (1393). The sequence of reactions occurred in the SBF different day immersion of bioactive glasses for various time periods are in favor of the formation of hydroxyapatite like layer on the surface of the samples [Hench et al.,



1998; Cortes et al., 1999 and Qiu et al., 1999]. In general, higher is the degradation higher would be the bioactivity. Therefore the titanium oxide doped glasses expected to be high bioactive. The samples Nos TiO<sub>2</sub>-1, TiO<sub>2</sub>-2 (wt %) were revealed most elevated pH among the others. The TiO<sub>2</sub>-1 and TiO<sub>2</sub>-2 contain 0.50 & 1.00 of titanium oxide possessed higher pH and on further addition of titanium 1.50 and 2.00 (wt %) showed lower pH values which might have delayed the release of alkaline ions from the glass. When TiO<sub>2</sub> is added in 1393 bio glass, glass structure is more open with increasing non bridging oxygen ions. Therefore more and more alkali and alkaline ions is released but the addition of more TiO<sub>2</sub> in glass, it produce the hindrance to the release of alkali and alkaline ions, this is why Ti<sup>4+</sup> doped bioactive glass shows slow release of alkaline ions. It was reported that the transition metal ions in 1393 bioactive glasses often showed a largely controllable dissolution property within physiological fluids and their exciting route for potential delivery systems within tissue regeneration scaffolds.

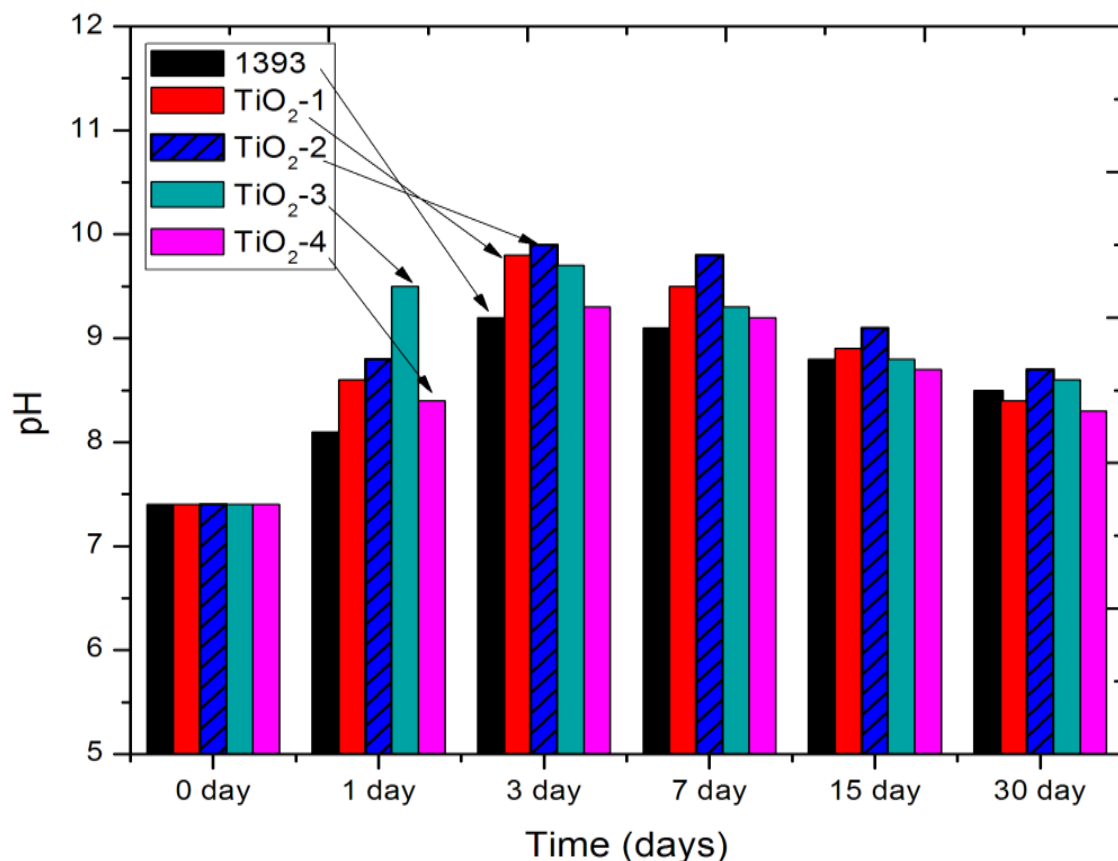
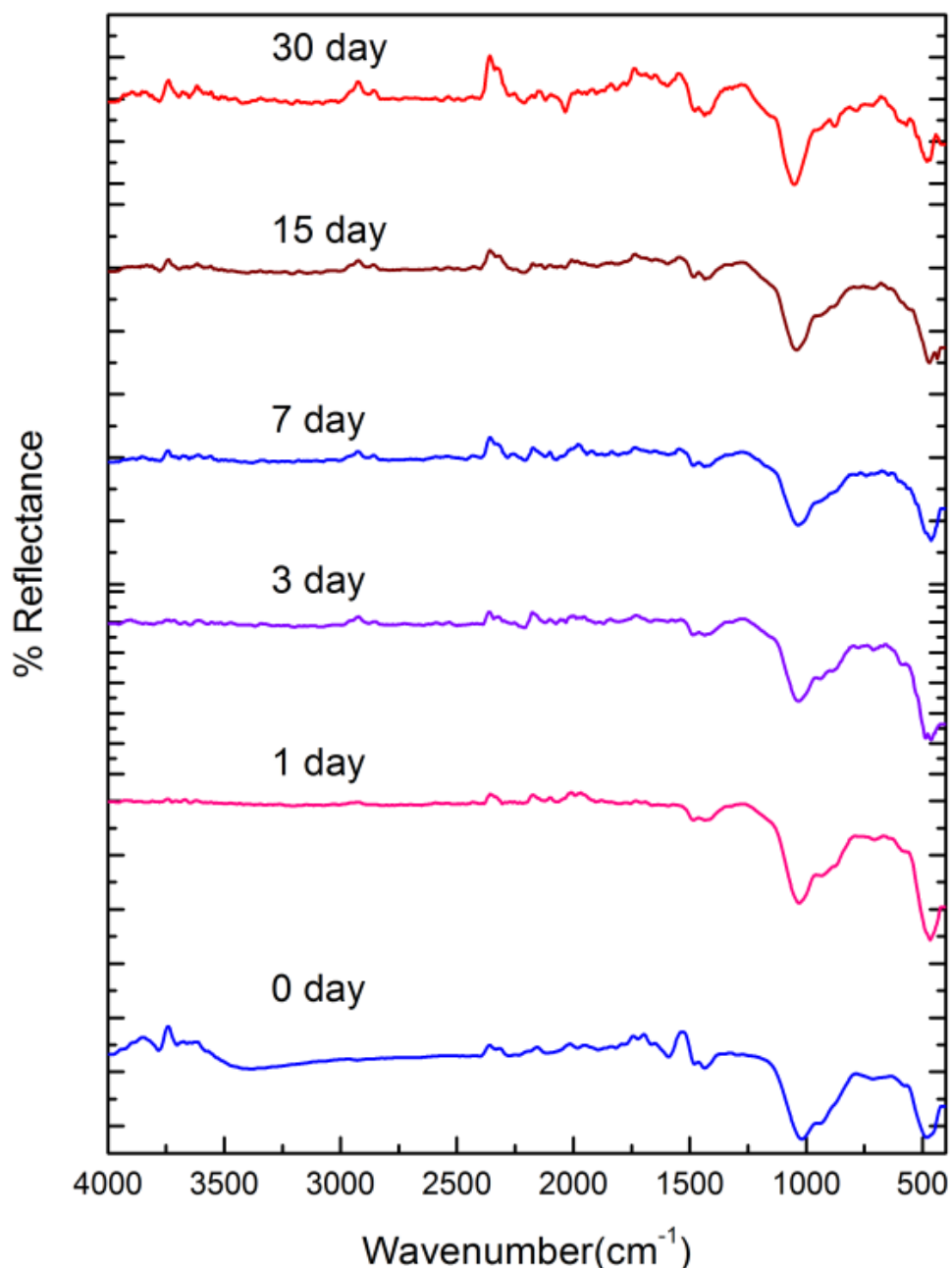


Figure 3.3- pH measurements of 1393 and titanium dioxide doped bioactive glasses

### 3.3.3 In vitro bioactivity of 1393 and doped bioactive glass by FTIR reflectance spectrometry

**Figure:** - 3.4, 3.5, 3.6, & 3.7 show the FTIR Reflection spectra bands of the bioactive glass before and after immersion in SBF for different days 0, 1, 3,7,15 and 30. Hench et al., 1998; Kim et al., 2000 and Filgueira et al., 2002 demonstrated that effect in the IR spectra bands after immersion in SBF for the protracted time period and the stages of apatite formation on the surface of the samples after immersion in SBF.



Figurer 3.4- FTIR reflectance spectra of TiO<sub>2</sub>-1

**Figure: - 3.4** shows the IR spectra bands of TiO<sub>2</sub>-1 sample before and after treated with SBF. The new bands have appeared after 1 day immersion in SBF when compared to before immersion at 596, and 690 cm<sup>-1</sup> corresponds to P–O bending (crystalline) and P–O bending (amorphous) bending respectively presence of C-O stretching 880 cm<sup>-1</sup> bond show the crystalline nature indicates the formation of hydroxyl carbonate apatite(HCA) layer. The bands at about 1431 and 1588 cm<sup>-1</sup> are associated with C-O (Stretch) and C=O (Stretch) stretching mode and the broadband at about 3772 cm<sup>-1</sup> can be assigned to (hydroxyl) O-H groups on the surface The protracted period of the samples in SBF shows the same behavior with small decrease in the intensities of the bands, which are resulted in favor of development of hydroxyl carbonated apatite (HCA) layer.

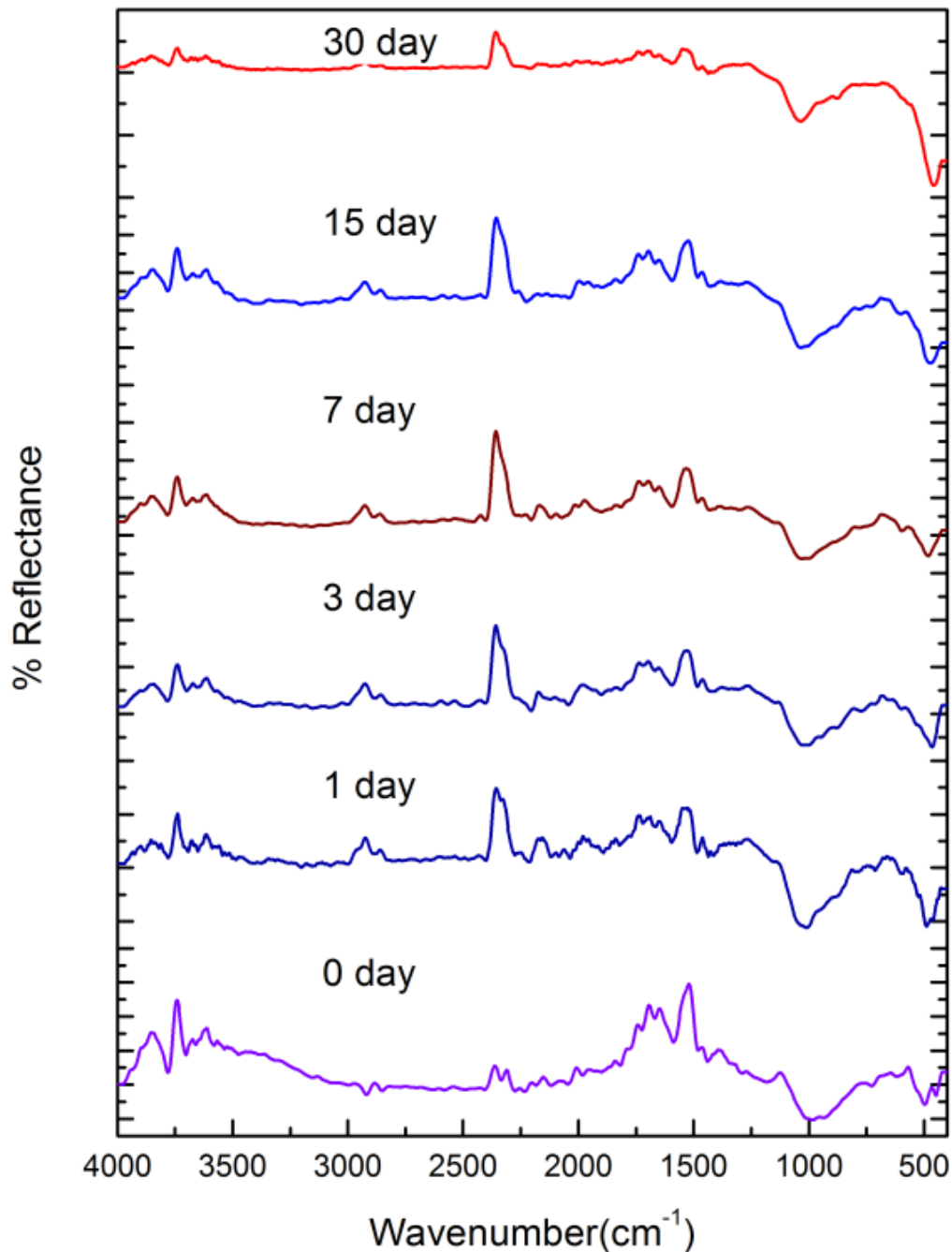
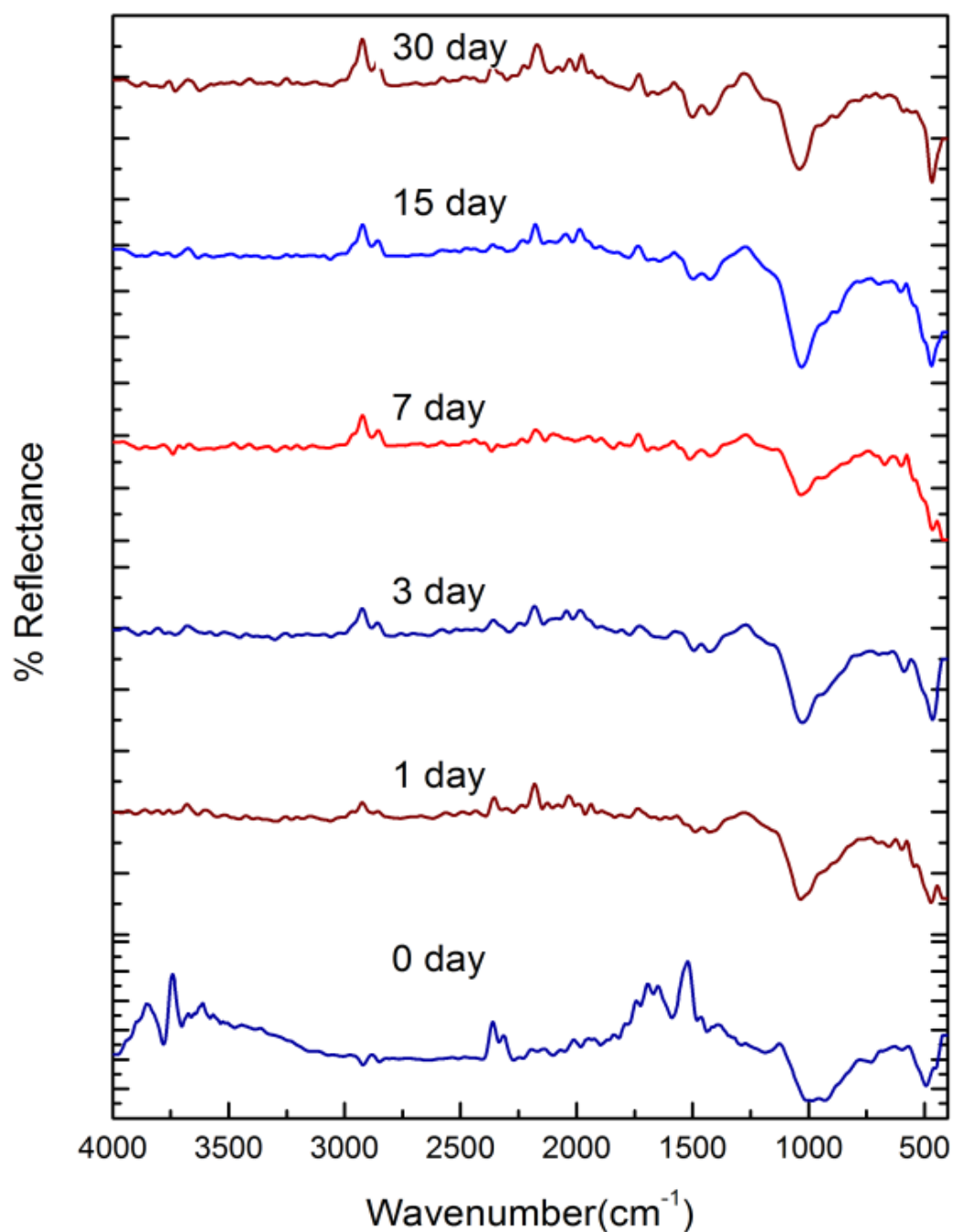


Figure 3.5- FTIR reflectance spectra of TiO<sub>2</sub>-2

**Figure: - 3.5** shows the IR spectra bands of TiO<sub>2</sub>-2 sample before and after treated with SBF. The new bands have appeared after 1 day immersion in SBF when compared to before immersion at 534, and 612 cm<sup>-1</sup> corresponds to P-O bending (crystalline) and P-O bending (amorphous) bending respectively presence of C-O stretching 880 cm<sup>-1</sup> bonds show the crystalline nature indicates the formation of

hydroxyl carbonate apatite(HCA) layer. The bands at about 1430 and 1589  $\text{cm}^{-1}$  are associated with C-O (Stretch) and C=O (Stretch) stretching mode and the broadband at about 3773  $\text{cm}^{-1}$  can be assigned to (hydroxyl) O-H groups on the surface. The protracted period of the samples in SBF shows the same trend with small decrease in the intensities of the bands, which are resulted in favor of development of hydroxyl carbonated apatite (HCA) layer.



Figurer 3.6- FTIR reflectance spectra of TiO<sub>2</sub>-3

**Figure: - 3.6** shows the IR spectra bands of TiO<sub>2</sub>-3 sample before and after treated with SBF. The new bands have appeared after 1 day immersion in SBF when compared to before immersion at 581, and 659 cm<sup>-1</sup> corresponds to P–O bending (crystalline) and P–O bending (amorphous) bending respectively presence of C-O stretching 862 cm<sup>-1</sup> bonds show the crystalline nature indicates the development of hydroxyl carbonate apatite(HCA) layer. The bands at about 1414 and 1588 cm<sup>-1</sup> are associated with C-O (Stretch) and C=O (Stretch) stretching mode and the broadband at about 3774 cm<sup>-1</sup> can be assigned to (hydroxyl) O-H groups on the fine surface The protracted period of the samples in SBF shows the same behavior with small decrease in the intensities of the bands, which are resulted in favor of development of hydroxyl carbonated apatite.

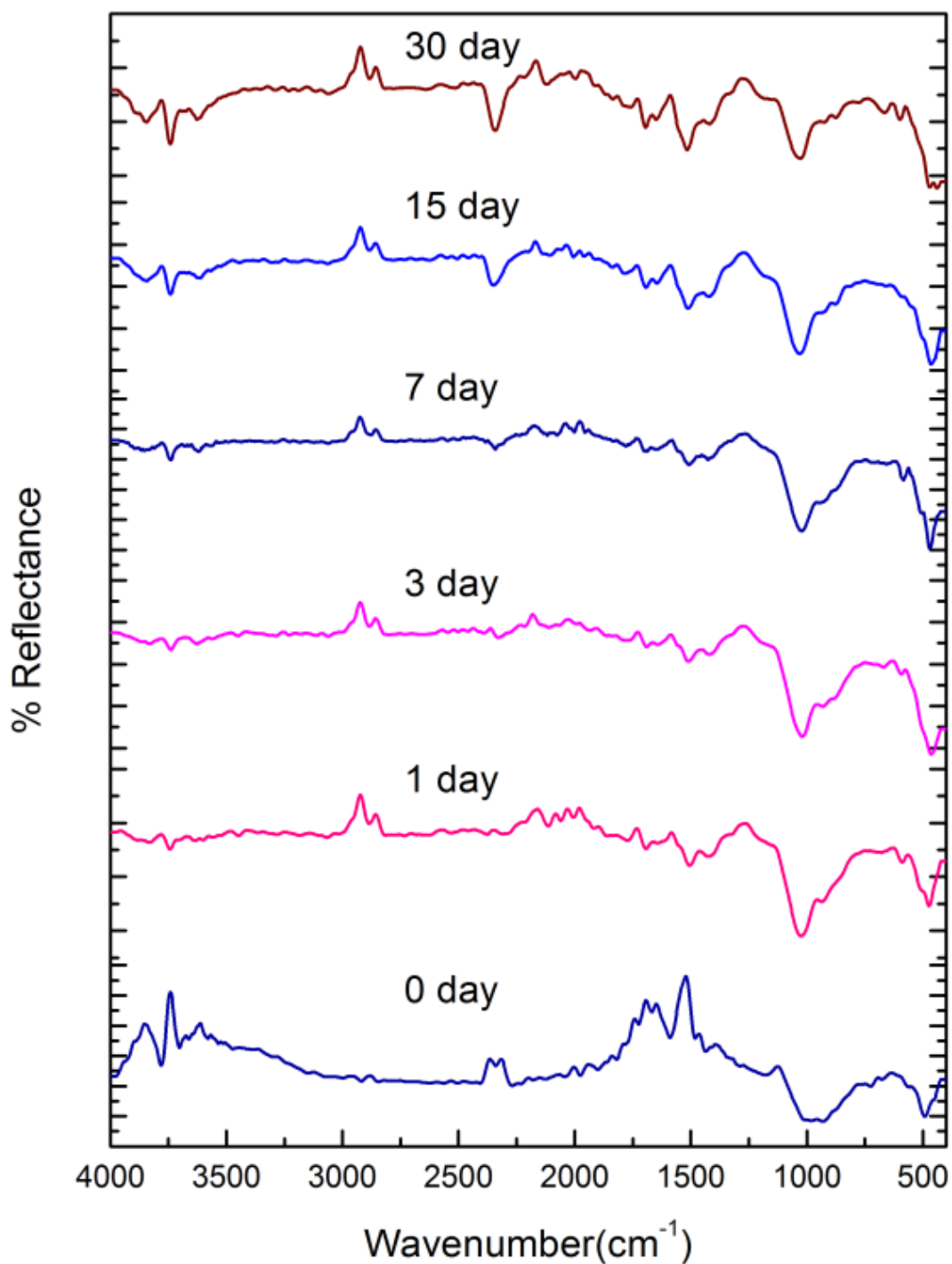


Figure 3.7- FTIR reflectance spectra of TiO<sub>2</sub>-4

**Figure:** - 3.7 shows the IR spectra bands of TiO<sub>2</sub>-4 sample before and after treated with SBF. The new bands have appeared after 1 day immersion in SBF when compared to before immersion at 565, and 559 cm<sup>-1</sup> corresponds to P–O bending (crystalline) and P–O bending (amorphous) bending respectively presence of C-O stretching 927 cm<sup>-1</sup> bonds show the crystalline nature indicates the development of

hydroxyl carbonate apatite(HCA) layer. The bands at about  $1494$  and  $1603\text{ cm}^{-1}$  are associated with C-O (Stretch) and C=O (Stretch) stretching mode and the broadband at about  $3775\text{ cm}^{-1}$  can be assigned to (hydroxyl) O-H groups on the surface. The prolonged period of the samples in SBF shows the same behavior with small decrease in the intensities of the bands, which are resulted in favor of development of hydroxyl carbonated apatite (HCA) layer.

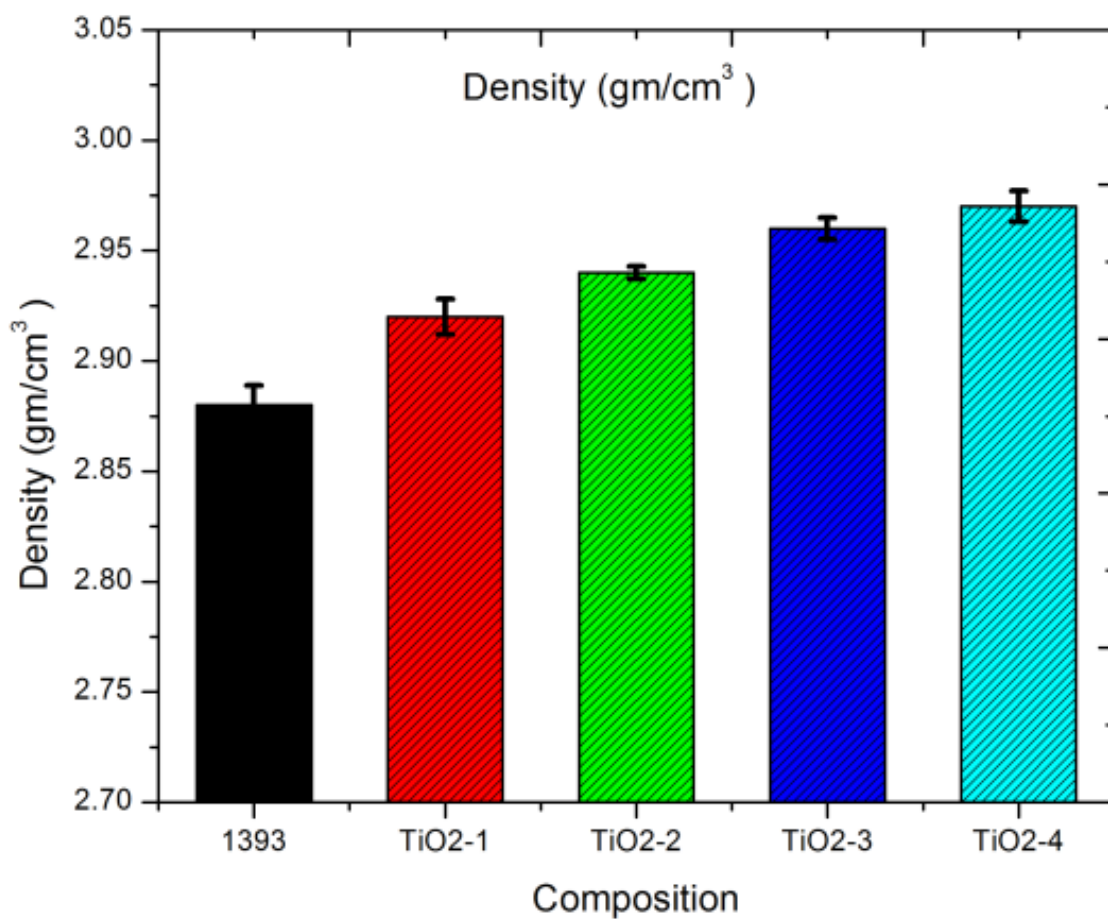


Figure 3.8- Density of bioactive glasses



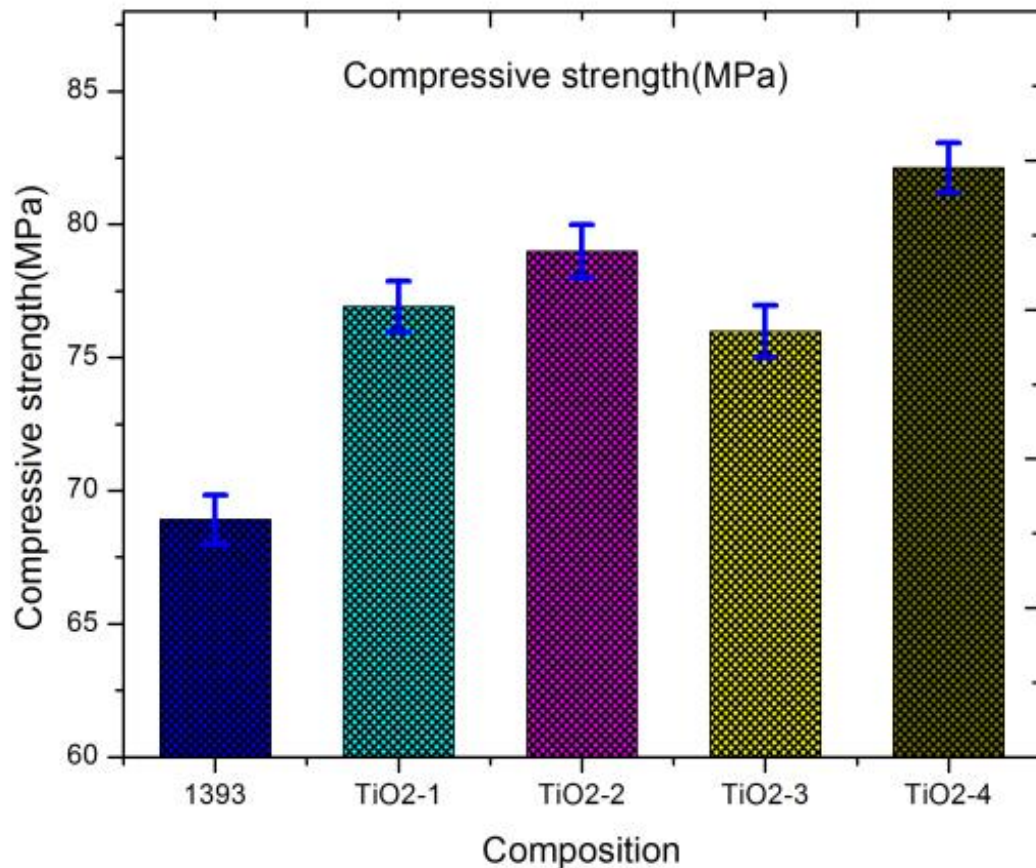


Figure 3.9- Compressive strength of bioactive glasses

### 3.3.4 Mechanical behavior 1393 and doped bioactive glasses

**Figure: - 3.8** show the density of titanium oxide doped 1393 bioactive glass. It is observed that the densities of the samples were increased with increasing titanium oxide content from 2.76 to 2.86 gm/cm<sup>3</sup>, which may be due to partial replacement of SiO<sub>2</sub> with TiO<sub>2</sub>, and is attributed due to the replacement of a light element (density of SiO<sub>2</sub> -2.64) with a heavier one (TiO<sub>2</sub>- 4.23). A similar trend of results also found in the compressive strength (1393, TiO<sub>2</sub>-1, TiO<sub>2</sub>-2, TiO<sub>2</sub>-3 and TiO<sub>2</sub>-4 and 67.62, 75.82, 76.62, 77.78 and 81.11 MPa respectively) shown in **Figure: - 3.9**.

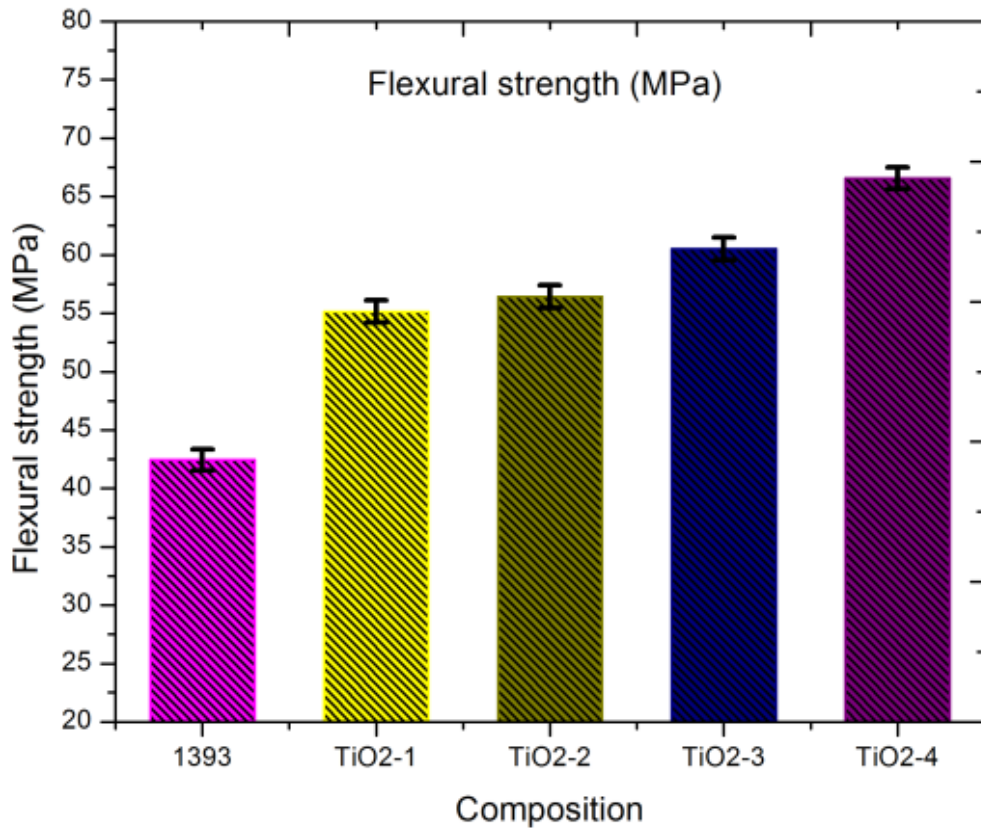


Figure 3.10- Flexural strength of bioactive glasses

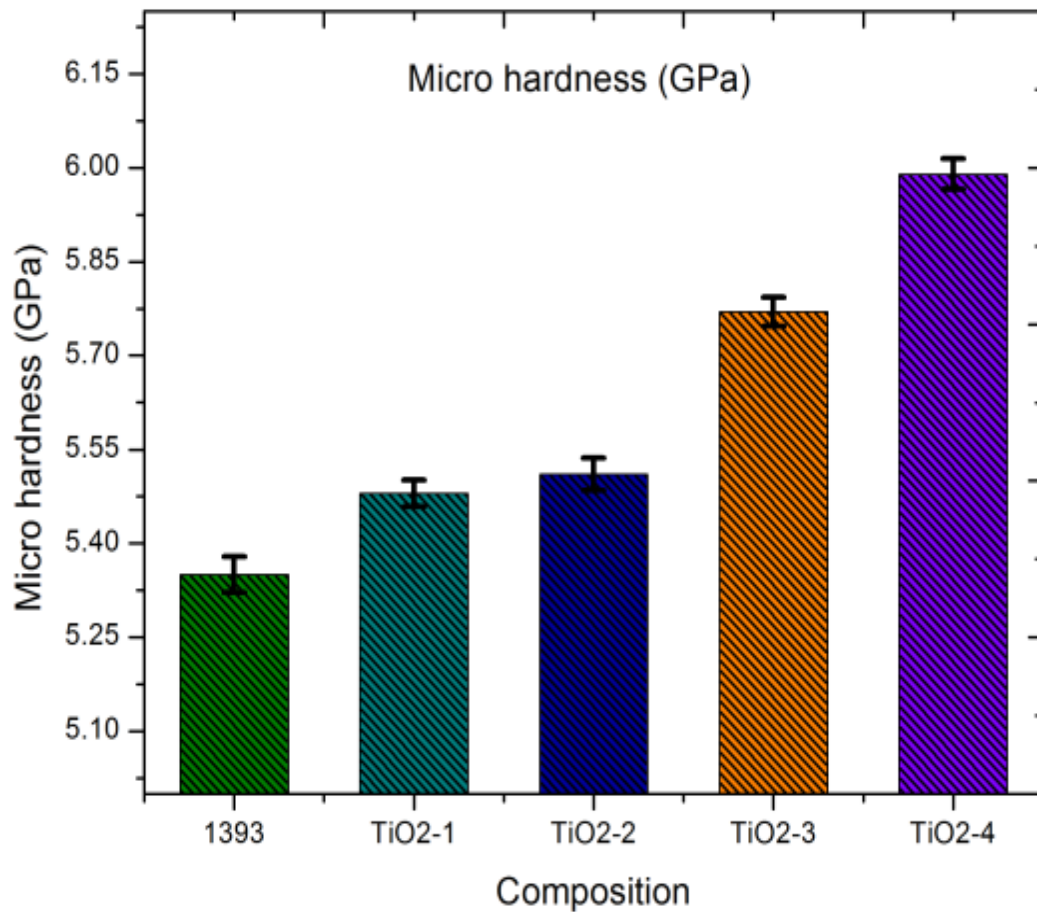


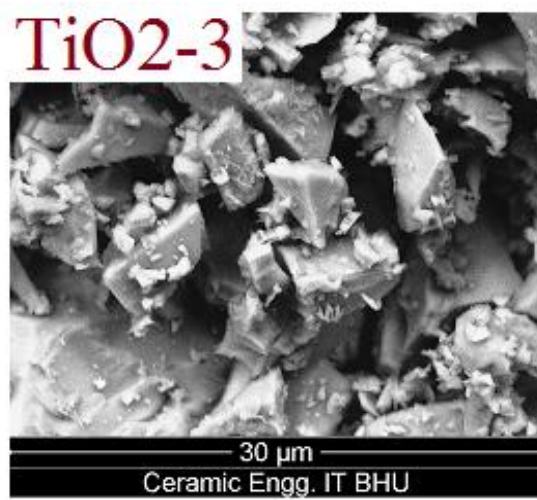
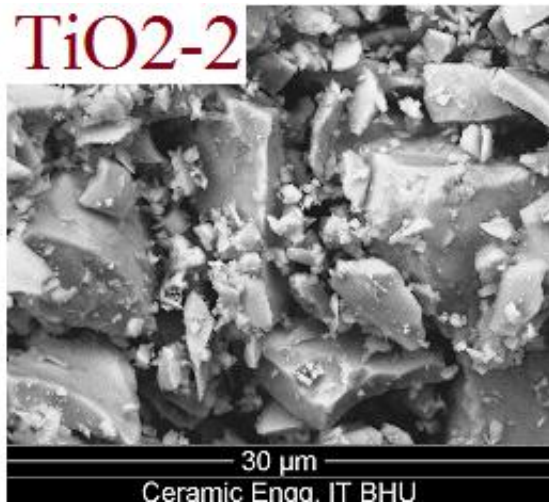
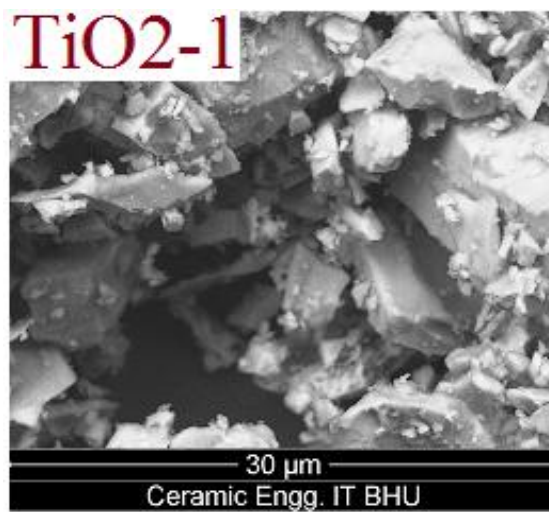
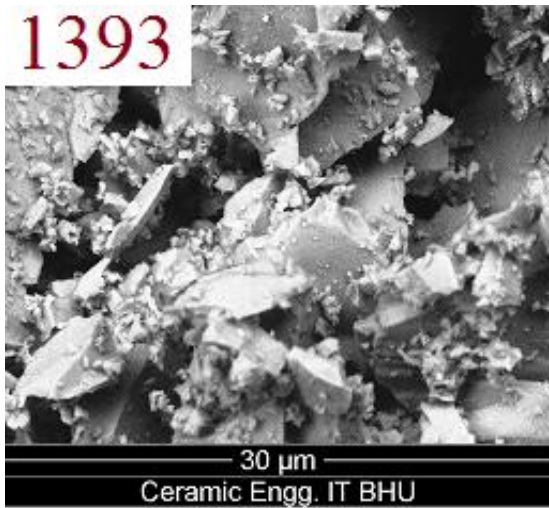
Figure 3.11- Micro hardness of bioactive glasses

**Figure: - 3.10 and 3.11** show the results of the flexural strength and Microhardness of 1393, TiO<sub>2</sub>-1, TiO<sub>2</sub>-2, TiO<sub>2</sub>-3, and TiO<sub>2</sub>-4 samples. The results demonstrate an increasing tendency in flexural strength and Microhardness as the percentage of titanium oxide increase (43.36, 54.75, 56.32, 59.22 and 63.42 Microhardness 5.25, 5.38, 5.41, 5.57 and 5.69) respectively. This increase may be due to the Ti<sup>2+</sup> may act as network intermediate, thus more the compactness of glass structure [Gehan et al., 2009]. When TiO<sub>2</sub> is added inn 1393 bioglass, glass structure is more open with increasing non bridging oxygen ions. Therefore more and more alkali and alkaline ions is released but the addition of more TiO<sub>2</sub> but the addition of more TiO<sub>2</sub> in glass it produce the hindrance the alkali and alkaline ions, this is why Ti<sup>4+</sup> doped bioactive glass shows slow release of alkaline ions. [Vyas et al., 2015] in an earlier investigation had also shown that the addition of cobalt oxide up to 2.0 wt% in 45S5 glass & glass-ceramic has resulted in an increase in density and compressive strength, flexural strength and Microhardness.

### 3.3.5 Scanning electron microscopy (SEM)

The SEM micrographs of 1393 glass and titanium oxide doped glass samples before immersing in SBF solution are shown in **Figure:- 3.12** which results in different rod types of structure and asymmetrical grain of 1393 bioactive glass samples and is quite similar to the results reported by [Hanan et al.,2009]. **Figure: - 3.13** represent the SEM micrographs of base glass and titanium oxide doped bioactive glass after immersed in SBF solution for 7 days. It is understandable from the **Figure: -3.13** that base and bioactive doped glass samples which were immersed in SBF solution for 7 days were

enclosed with an asymmetrical shape and grounded HA particles have been grown into more than a few agglomerates consisting of spine shaped HA layer. These micrographs show the formation of HA on the surface of the base and 1393 bioactive doped glass samples after immersion in SBF solution for 7 days [Tadashi et al., 2003].



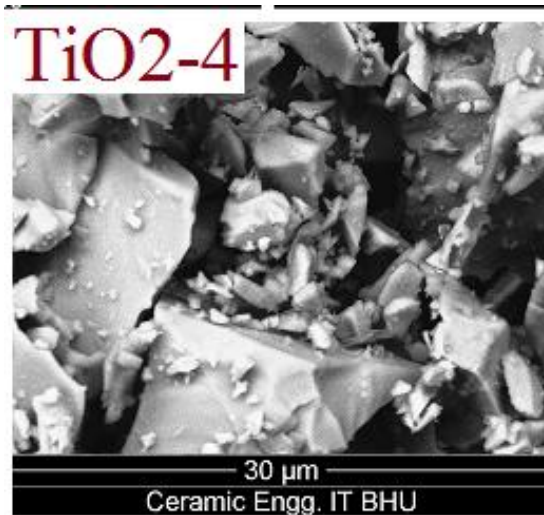
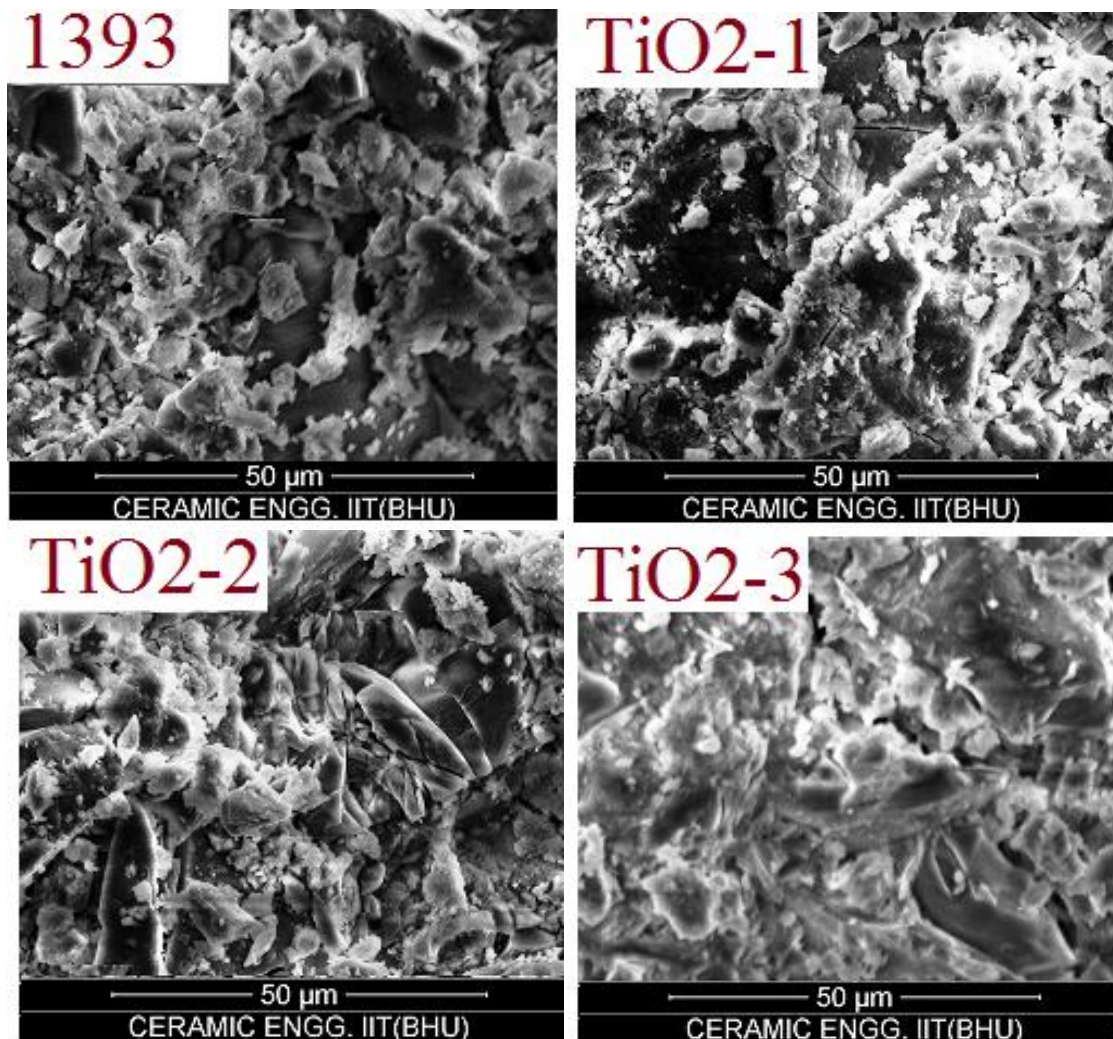


Figure 3.12- Scanning electron microscope (SEM) of bioactive glasses before immersion in SBF



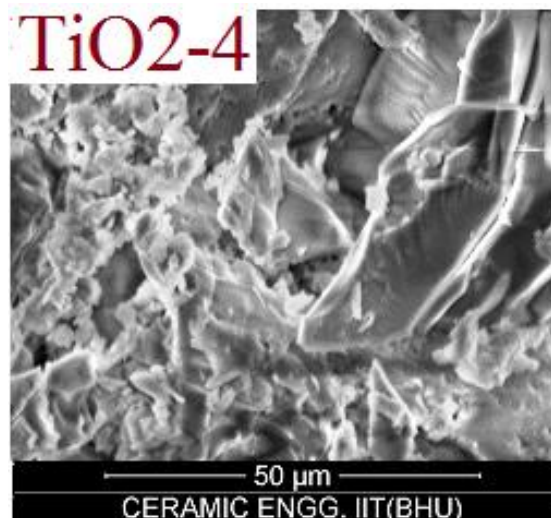


Figure 3.13- Scanning Electron Microscope (SEM) of bioactive glasses after immersion in SBF for 7 days

### 3.4 CONCLUSIONS

In the present investigation, a comparative investigation was made on physicomachanical and bioactive properties of titanium oxide doped 1393 bioactive glasses. The following conclusions were drawn from this investigation. It is concluded that an increase in titanium oxide content in this series of glasses resulted in an increase in bioactivity. This is also supported by pH and SEM analysis. FTIR results showed the silicate network structure in prepared bioactive glass and increasing the titanium oxide content in 1393 bioactive glass increase the density, flexural strength, compressive strength, and microhardness.