Structural and elastic properties of Strontium doped Phosphate bioactive glasses

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Abstract

Bioactive glasses are a class of biomaterials which have the potential of becoming suitable candidates for osteogenesis. The glasses made with phosphate as the former have exceptional properties. The functional characteristics are due to the lower values of viscosity and dispersion and higher values of refractive indices. These glasses show high transparency in the range of UV spectrum. Inclusion of oxides first group and second group elements i.e., alkali and alkaline earth metal oxides respectively into the glass network modify the properties and increase the chemical resistance of phosphate glasses. Different compositions of strontium doped phosphate glasses were prepared using melt quench technique. X – Ray Diffraction (XRD) studies were performed in order to confirm the amorphous nature . The effect of adding modifier into the glass matrix was evaluated using FTIR characterization. The elastic parameters like moduli and Poisson's ratio were calculated using Makishima and Mackenzie model. It was validated that modifiers have a significant impact on glass structure and bioactivity. These glasses are found to be capable in reducing burden on metallic biomaterials for osteogenesis and hence contribute for sustainable environment.

Keywords: phosphate glasses, osteogenesis, FTIR, elastic moduli

1 Introduction

Solids lacking order for long range in arrangement are called as non – crystalline solids. These solids are sometimes termed as glass and some other times are called as amorphous solids when non – conventional methods like vapor deposition, sol gel etc are employed for the synthesis. Unlike crystals, amorphous materials lack the long range translational order (periodicity). The terms 'amorphous' and 'non-crystalline solids' are used in the same meaning in this context (1; 2; 3; 4).

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Glasses are a class of amorphous materials which can be synthesized with materials that form different chemical bonds such as ionic bond, covalent bond, metallic bond, hydrogen bond, Van der Waals bond or a combination of these bonds. By altering the chemical composition, a wide range of glasses with many components can be created with the appropriate composition. The combination of a dopant salt, a network former, and a network modifier in various ratios results in the diverse chemical components of a glass. Also, such systems are observed to form glasses more readily. When cations are added to the glass network, the Bridging Oxygens (BOs) get converted to Non Bridging Oxygens (NBOs). The network then undergoes depolymerization as a result of this. The changes to the characteristics can be attributed to this change.

Bone grafts, implant coatings etc are made because of which bioactive glasses gain immense importance (5; 6; 7; 8; 9). The first bioactive glass 45S5 Bioglass® was developed by Hench (10). It had the composition 46.1 SiO_2–2.6 P_2O_5–24.4 Na_2O–26.9 CaO (mol%) (11). In recent times, phosphate glasses have gained importance owing to lot of scientific implications such as sensors, solid state batteries (12; 13). Their viscosity and dispersion are less whereas they have high refractive indices. In the UV range, they show high transparency making the functional properties interesting (14; 15). The chemical strength of the phosphate glasses can be enhanced and the properties can be altered by the addition of alkali and alkaline earth metal oxides into the glass network (16).

The building blocks of these glasses are PO_4 – tetrahedral which originate from the formation of sp^3 hybrid orbitals (17). In the glass system under consideration, CaO, Na_2O and SrO are modifiers and P_2O_5 is a glass former.

Strontium is of paramount significance in biomedical science (18), predominantly because of its impact on bone growth. Even though occurs naturally in human body, the quantity is meagre. Around 99% of Strontium in body is found in bone enabling it to behave as “bone seeker” like calcium (19). Along with calcium and sodium, Strontium contributes for the formation of bone (20).

There is a necessity to know the structural, transport, and optical features to decide the possible application of glasses. Infrared spectroscopy is te significant analytical tool for examining the structure of glasses. It is one of the useful methods for figuring out how glasses vibrate. Makishima and Mackenzie model is found to be good theoretical model to predict the elastic paramaters of glasses. The structural and elastic characteristics of strontium-doped phosphate bioactive glasses are studied in this article.

2 Experimental

2.1 Glass preparation

Glasses of composition 45P_2O_5- xCaO- (50-x)Na_2O- 5SrO with x = 20, 25, 30, 35mol% were prepared by conventional melt-quenching technique. Weights of chemicals to be used were calculated using Batch matrix calculator and weighed accordingly. To homogenize the mixture, the chemicals were finely ground in an agate mortor. The mixture of chemicals was placed in a porcelain crucible inside a muffle furnace and heated upto 1050 $^{\circ}C$. The melts were quenched using brass plates to obtain the glasses. To eliminate the air bubbles and thermal stresses developed during the process of quenching, the synthesized glasses were subjected to annealing at 200°C for roughly 2 hours. Table 1 consists of composition of glasses.

TABLE 1

Chemical compositions of glasses

Sample code	CaO mol%	Composition
Sr1	20	45P_2O_5- 20CaO- 30 Na_2O- 5SrO
Sr2	25	45P_2O_5- 25CaO- 25 Na_2O- 5SrO
Sr3	30	45P_2O_5- 30CaO- 20 Na_2O- 5SrO
Sr4	35	45P_2O_5- 35CaO- 15 Na_2O- 5SrO

2.2 XRD Analysis

Rigaku Ultima 4 PXRD instrument was employed to the X – Ray Diffraction for the synthesized glass samples which were crushed to fine powder. The XRD spectrum was obtained for the diffraction angle 2θ ranging between 10° and 80°.

2.3 Density and Molar Volumes

In order to determine the density of the glasses, their weights were measured in air and after immersing in toluene ($\rho_{toulene}$= 0.860 g/cm^3). Microbalance (Denver, Pb214) with 4 digit sensitivity was used for weight measurements. Then, the density 'ρ' was determined on the basis of Archimedes principle using the relation

$$\rho = \frac{W_a}{W_a - W_t}\rho_t$$

where W_a is the glass sample's weight in air

W_t is the glass sample's weight in toluene

ρ_t is the density of toulene (ρ_t = 0.860 g/cm^3).

The molar volume (V_M) was calculated using the following relation,

$V_M = M/\rho$ (2)

where M is the molecular weight.

2.4 Fourier Transform Infrared spectroscopy

Fourier Transform Infra-Red (FTIR) spectroscopy is an important practical tool for understanding the bonding mechanisms and the unique vibrational chemical bond frequencies that cause spectral and structural changes. The absorption spectra of the glasses in the IR region were recorded in the range of 2000 – 400 cm^{-1} using an FTIR reflectance spectrometer (TENSOR 27, Bruker, Germany) at room temperature.

2.5 Calculation of Elastic Moduli

Elastic characteristics of materials are important as they reveal information about the forces interacting between the atoms. This is crucial for analysing and comprehending the nature of solid-state bonding. Also, knowledge of mechanical qualities of materials is necessary for understanding the strength, ductility and applications. Therefore, as a function of composition, elastic characteristics are appropriate for defining the glass structure. The elastic moduli of oxide glasses can be determined theoretically by making use of experimentally determined density values with the help of the Makishima and Mackenzie model (21; 22). According to this model, the semi empirical formulae are derived to calculate elastic parameters and Poisson's ratio.

The formulae are as follows:

Packing density $V_t = \frac{\rho}{M}\sum_i V_i x_i$ (3)

Dissociation energy per unit volume $G_t = \sum_i G_i x_i$ (4)

where x_i is the molar fraction

V_i is the packing factor

G_i is the dissociation energy per unit volume of the component oxide i,

ρ is the density of the glass

M Is the molecular weight of the glass, respectively

The packing factor and dissociation energy per unit volume of a component oxide i in the form A_nO_m can be estimated from its dissociation energy per mole (U_i), density (r_i) and molec-

ular weight (M_i), according to the following equations:

$$V_i = \frac{4}{3}\pi N_A(nR_A^3 + mR_O^3)$$

$$G_i = \frac{\rho_i}{M_i}U_i$$

where R_A is Pauling's ionic radius of metal

R_O is Pauling's ionic radius of oxygen

N_A is Avogadro's number.

Using the calculated values of V_t and G_t, moduli of elasticity are determined using the subsequent relations:

Young's modulus $E = 8.36V_tG_t$ (7)

Bulk modulus $K = 10.0\ V_t^2G_t$ (8)

Shear modulus $G = \frac{3K}{(10.2V_t - 1)}$ (9)

Longitudinal modulus $L = K + \frac{4G}{3}$ (10)

Poisson's ratio $\sigma = 0.5 - (\frac{1}{7.2V_t})$ (11)

If G_t is expressed in terms of kcal/cm^3, then the elastic moduli obtained using equations (7) to (11) will be in GPa (23).

2.6 Bioactivity studies (in vitro)

Preliminary investigation of bioactivity of these glasses was done by immersing one sample Sr3 in Simulated Body Fluid (SBF) for 3, 7, 14 and 21 days and kept inside the incubator at about $37°C$. SBF is a solution whose pH is almost equal to pH of human body i.e., 7.4. The glass samples were removed after the prescribed duration, dried and was subjected to XRD analysis.

3 Results and Discussions

3.1 Density and Molar Volumes

The change in density and molar volumes with increase in CaO mol% is represented in Fig 1. It can be seen from figure 1 that the density increases while molar volume decreases with CaO mol%. The results on the density of calcium phosphate glasses show the similar trend of increase in density (24). The error is found to be around 0.18% based on the relative instrumental error. Non-bridging oxygens (NBOs) are formed in the glass matrix as a result of

TABLE 2

Density and molecular weight of glasses

Physical Property	Glass Sample Code			
	Sr1	**Sr2**	**Sr3**	**Sr4**
Density ρ (g/ cm^3)	2.6190	2.6725	2.7260	2.7795
Molar Volume V_M (cm^3)	37.28877	36.31974	35.38874	34.49358

both the modifiers CaO and Na_2O. The concentration of Strontium Oxide is kept constant. With gradual increase of CaO, the NBOs formed will consist of isolated PO_4 tetrahedron bonds linked together by ionic CaO bonds as the concentration of SrO is kept constant. The density of SrO ($4.7 g/cm^3$) is more than that CaO($3.34 g/cm^3$) which is also the reason for the higher density of the glasses. Consequently, the increase of the calcium content leads to increase in the quantity of the non-bridging oxygens. This causes a decrease in the free space in the glass network structure resulting in the increase of density from 2.6190 gcm^{-3} to 2.7795 gcm^{-3} and decrease in the molar volume from 37.2887 cm^3 to 34.4935 cm^3. Hence, changes in the structure of the phosphate units in the glass samples are credited to the NBOs (25).

3.2 X — Ray Diffraction

3.3 FTIR spectra

Figure 3 represents the FTIR spectra of glass samples and the assignment of bands with their characteristic frequencies is given in table 3.

Kordes et al. (26; 27) explained the formation of non-bridging oxygen, NBOs, in phosphate glasses. The formation of different phosphate structural groups during the processes of reorganization with the addition of modifier oxide was also explained. It was assumed that the doubly bonded oxygen would persist and that the number of NBOs produced would be directly proportional to the amount of alkali supplied. The three-dimensional network gets converted to linear phosphate chains when Na_2O or CaO to P_2O_5 are added to glasses (28; 29). It is an established fact that, with increase in modifier concentration in the phosphate matrix (30).

The broad band at ~1265 cm^{-1} is designated to the asymmetric stretching due to vibration of doubly bonded Oxygen atom (31). The absorption band at ~1105 cm^{-1} is assigned to the movement of the NBOs (PO_3) and that at ~898 cm^{-1} is because of the asymmetric stretching of P-O-P groups (32). The rise in intensity of the band 715 - 726 cm^{-1} at the expense of bands ~ 752 cm^{-1} and 775 cm^{-1} seems to indicate the conversion of structural units which is happening with increasing Na_2O content (33). The bands between 400 and 600 cm^{-1}correspond

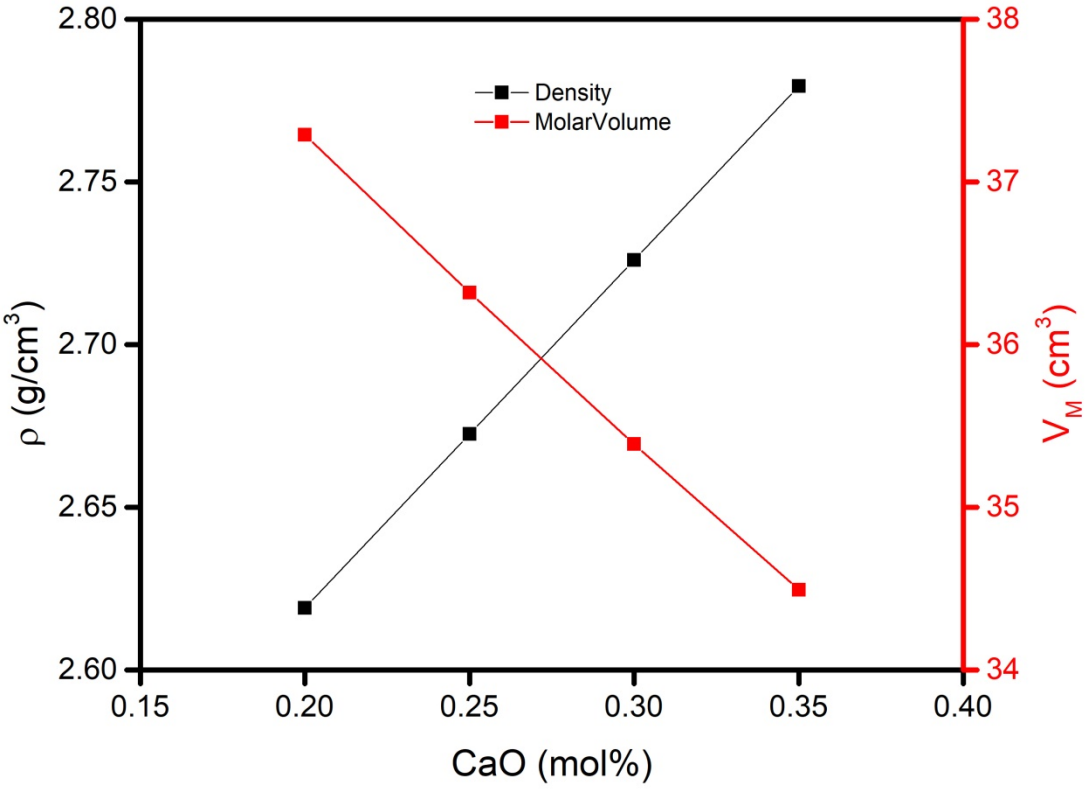

FIGURE 1

Variation of density and molar volume

to the bending vibrations of bridging phosphorous. The inclusion of an alkaline earth oxide depolymerizes the glass network (34). The depolymerization of the network into theoretically infinite chains is caused due to addition of divalent cation. This observation is consistent with the decrease in molar volume.

3.4 Results on elastic moduli

The variation of elastic moduli and Poisson's ratio with increase in CaO mol% are given in figure 4 and 5 respectively. It can be observed that elastic moduli and Poisson's ratio increase linearly with increase in mol% of CaO. The value of σ is between 0.25896 and 0.27407. The increment of σ value by 0.022 (approximately) is attributed to the modification of network caused by increase in CaO content which acts as modifier. This results in rise of phosphate linkage which in turn decreases the lateral strain.

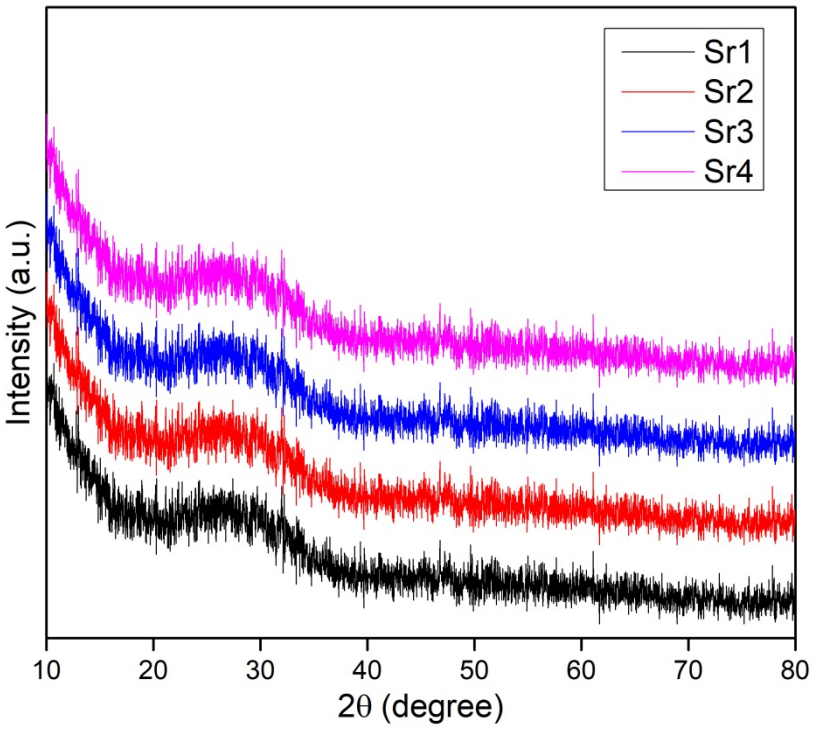

FIGURE 2

XRD spectra of glass samples

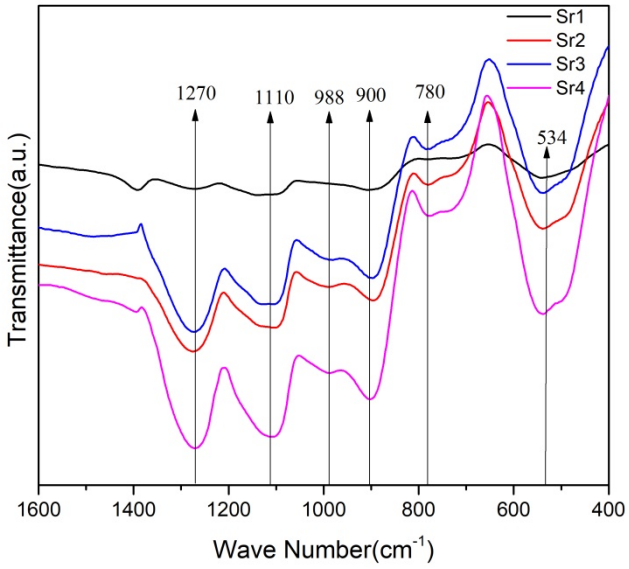

FIGURE 3

FTIR spectra of samples

TABLE 3

IR band assignments in the range of 400 – 1600 cm-^{1}[f] or glass samples

Range frequency (cm^{-1})	Band assignment
458 - 680	Bending vibrations of O-P-O and/or P=O bridges, δ(O-P-O) and/or δ(P=O)
715 - 830	P – O – P bridges' symmetric stretch, υ_s (P-O-P)
880 - 1022	P-O-P bridges' asymmetric stretch in metaphosphate configurations , υ_{as} (PO_2^-)
~1100	P-O-P bridges' asymmetric stretch in pyrophosphate configurations, υ_{as} (PO_3^-)
~1200	P=O bonds' symmetric stretch , υ_s (P=O)
1260 – 1340	P=O bonds' asymmetric stretch, υ_{as} (P=O)

Increase in density will cause the increase of ultrasonic velocities in the glass samples thereby leading to increase in elastic moduli which is evident in the results. This trend is in good agreement with the density and molecular weights of glass samples (35).

3.5 Results on bioactivity studies

The XRD spectra of Sr3 glass sample post bioactivity test is given in figure 6.

Hydroxyapatite (HA) is a naturally occurring phosphate mineral that is found in bones. The bioactivity of glass samples is verified with the formation of HA on the glasses when immersed in SBF. The sharp peak at around 32 in the XRD spectra for 14 and 21 days corresponds to HA [36-37] (36). The intensity of the peak corresponding to the crystalline phases of all the samples is observed to increase with time indicating that the formation of HA on the surface of the glass happens when they are immersed in SBF for longer duration.

4 Conclusions

The physical and structural properties of strontium doped phosphate bioactive glasses have been examined. The properties were examined by altering the contents of Na_2O and CaO prepared by conventional melt quench technique. This structural modification of the glass network led to an increase in the density and decrease in the molar volume. The FTIR spectra confirm the characteristic vibrational modes of phosphate groups. The elastic moduli and Poisson's ratio

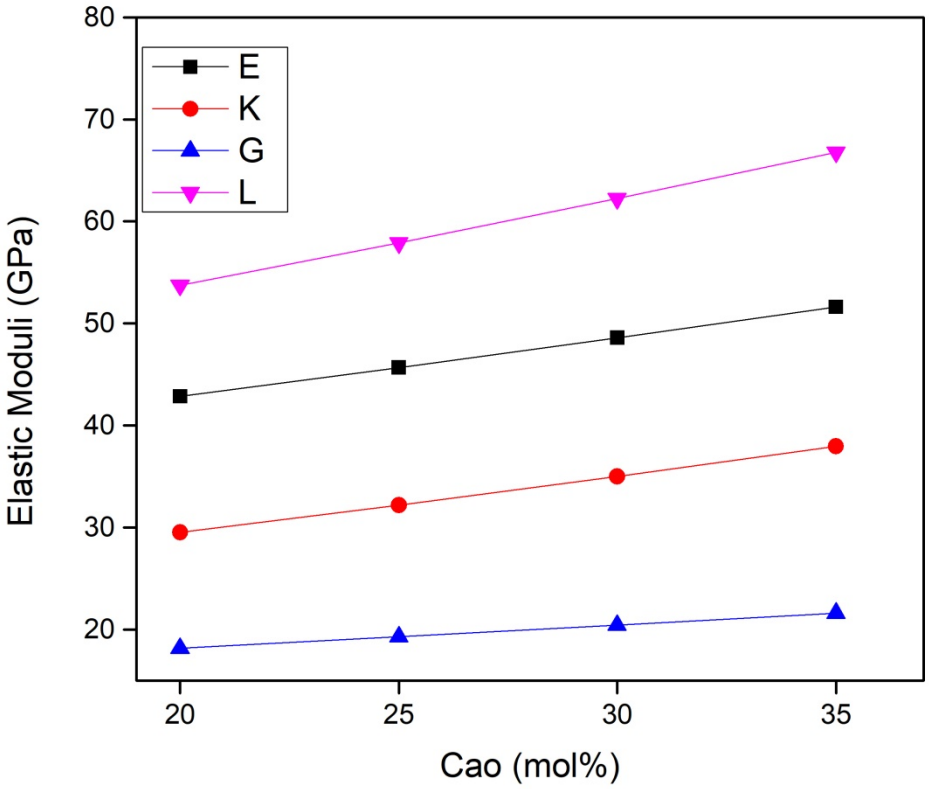

FIGURE 4

Variation of elastic moduli with CaO mol%

values are consistent with the density values. It is obvious from the elastic parameters that the glass material synthesized has good rigidity. Substitution of CaO with Na_2O has produced a significant increase in the structural and elastic properties of these glasses.This glass system is subjected to in vitro bioactivity studies by immersion in SBF. The preliminary investigation has yielded positive results. The presence of strontium in the matrix is expected to enhance the bioactivity of these glasses and hence support for growth of osteogenic tissues.

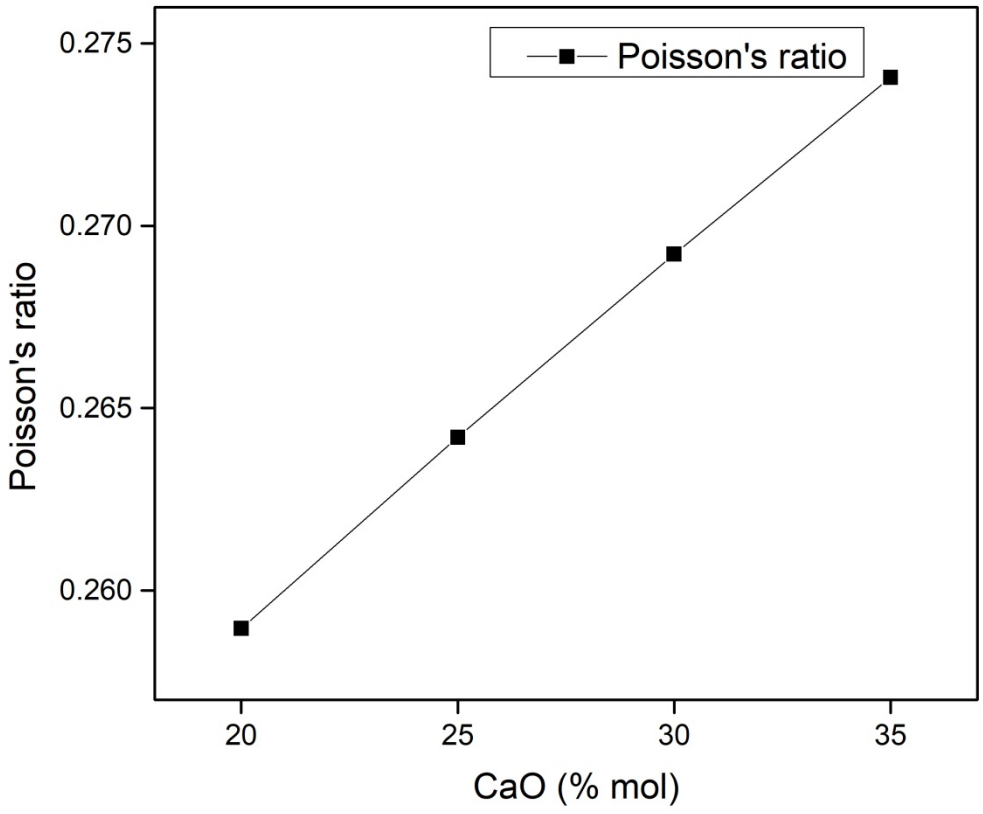

FIGURE 5

Variation of Poisson's ratio with CaO mol%

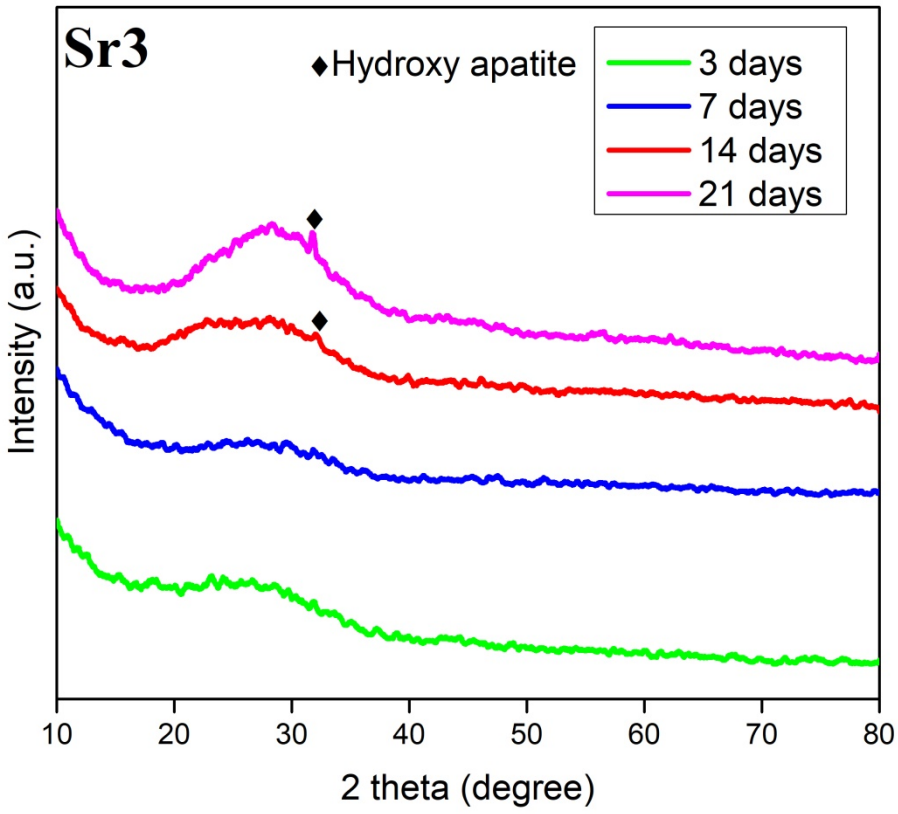

FIGURE 6

XRD of Sr3 post immersion in SBF

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References

[1] S R Elliott. *Physics of Amorphous Materials*, pages 6–6, 1990.

[2] J Zarzycki. Glasses and the vitreous state. pages 8–8, 1991.

[3] H Scholze. Glass: Nature, structure and properties. pages 121–121. Springer, 1991.

[4] A K Varshneya, Fundamentals of Inorganic Glasses, 1994.

[5] L L Hench. *J. Am. Ceram. Soc*, 81:1705–1728, 1998.

[6] J M Gomez-Vega, E Saiz, A P Tomsia, T Oku, K Suganuma, and G W Marshall. *Novel bioactive functionally graded coatings on Ti6Al4V*, 12:894–898, 2000.

[7] N Lotfibakhshaiesh, D S Brauer, and R G Hill. Bioactive glass engineered coatings for Ti6Al4V alloys: influence of strontium substitution for calcium on sintering behaviour. *J. Non-Cryst. Solids*, 356:2583–2590, 2010.

[8] M R Towler, C M Crowley, D Murphy, and A M C O'callaghan. A preliminary study of an aluminium-free glass polyalkenoate cement. *J. Mater. Sci. Lett*, 21:1123–1126, 2002.

[9] B J Tai, Z Bian, H Jiang, D C Greenspan, J Zhong, and A E Clark. Anti-gingivitis effect of a dentifrice containing bioactive glass (NovaMin (R)) particulate. *J. Clin. Periodontol*, 33:86–91, 2006.

[10] L L Hench. *An Introduction to Bioceramics*. World Scientific Publishing Company, Singapore, 1993.

[11] M I Abdel-Ati and A A Higazy. Electrical conductivity and optical properties of gamma-irradiated niobium phosphate glasses. *J. Mater. Sci*, 35:6175–6175, 2000.

[12] Himanshu Tripathia, Chandana Rathb, Arepalli Sampath Kumara, Partha Pratim Mannac, and S P Singh, Structural, physico-mechanical and in-vitro bioactivity studies on SiO2-CaO-P2O5-SrO-Al2O3 bioactive glasses. https://doi.org/10.1016/j.msec.2018.09.041

[13] S Hraiech. *Journal of Non-Crystalline Solids*, 2017.

[14] T I Suratwala, R A Steele, G D Wike, J H Campbell, and K Takenchi. Effects of OH content, water vapor pressure and temperature on sub-critical crack growth in phosphate glass. *J. Non-Cryst. Solids*, 263:213–213, 2000.

[15] R Praveena, V Venkatramu, P Babu, and C K Jayasankar. Fluorescence spectroscopy of Sm3+ ions in P2O5-PbO-Nb2O5 glasses. *Physica B*, 403:3527–3527, 2008.

[16] R Brow and D Tallant. Structural design of sealing glasses. *J. Non - Cryst. Solids*, 222:396–406, 1997.

[17] K Richard and Brow. Review: the structure of simple phosphate glasses. *Journal of Non - Crystalline Solids*, 263:1–28, 2000.

[18] S P Nielsen. The biological role of strontium. *Bone*, 35:583–588, 2004.

[19] J K Christie and N H De Leeuw. Effect of strontium inclusion on the bioactivity of phosphate-based glasses. *J Mater Sci*.

[20] E Bonnelye, A Chabadel, F Saltel, and P Jurdic. Dual effect of strontium ranelate: stimulation of osteoblast differentiation and inhibition of osteoclast formation and resorption in vitro. *Bone*, 42:129–138, 2008.

[21] A Makishima and J D Mackenzie. Direct calculation of Young's modulus of glass. *J. Non Cryst. Solids*, 12:35–45, 1973.

[22] A Makishima and J D Mackenzie. Calculation of bulk modulus, shear modulus and Poisson's ratio of glass. *J. Non-Cryst. Solids*, 17:147–157, 1975.

[23] Abd El-Moneim, A Alfifi, and H Y. Approach to dissociation energy and elastic properties of vanadate and V2O5-contained glasses from single bond strength: Part I. *Materials Chemistry and Physics*, 207:271–281, 2018.

[24] Z A Talib, W M Daud, E Z M Tarmizi, H A A Sidek, and W M M Yunus. Optical absorption spectrum of Cu2O - CaO - P2O5 glasses. *J. Phys. Chem. Solids*, 69(8):1969–1973, 2008.

[25] M Chethan, & Reddy, M & Abhiram, and Asha Rajiv. Optical Properties of Calcium Sodium Phosphate Glasses Doped With Strontium. *Journal of Physics: Conference Series*, 241:1–1, 1939.

[26] E Kordes, W Vogel, and R Feterowsky. *Z. Electrochem*, 57(4):282–282, 1953.

[27] B C Bunker, G W Arnold, and J A Wilder. *J. Non-Cryst. Solids*, 64:291–291, 1984.

[28] Y B Peng and D E Day. *Glass Technol*, 5:166–166, 1991.

[29] Paramjyot Kumar Jha, O P Pandey, and K Singh. FTIR spectral analysis and mechanical properties of sodium phosphate glass-ceramics. *Journal of Molecular Structure*, 1083, 2015.

[30] B V R Chowdari, K I Tan, W T Chia, and R Gopalakrishnam. *J. Non-Cryst. Solids*, 119:95–102, 1990.

[31] A Shaim and M Et-Tabirou. *Mat. Chem. Phys*, 80:63–67, 2003.

[32] A A Kader, A A Higazy, and M M Elkholy. *J. Mater. Sci.: Matter. Electron*, 2(3):157–163, 1991.

[33] S Ferraa, H Barebita, M Moutataouia, A Nimour, A Elbadaoui, B Baach, and T Guedira. Effect of barium oxide on structural features and thermal properties of vanadium phosphate glasses. *Chemical Physics Letters*, 765:138304–138304, 2021.

[34] M Venkata Subba Reddy, M Reddy, C Reddy, and R P S Chakradhar. Elastic properties of Na2O-B2O3-V2O5 glasses. *Journal of Alloys and Compounds*, 479:17–21, 2009.

[35] Sakthi Prasad, S, Susmit Datta, Tarun Adarsh, K Prerna Diwan, Biswanath Annapurna, Kaushik Kundu, and Biswas. Effect of boron oxide addition on structural, thermal, in vitro bioactivity and antibacterial properties of bioactive glasses in the base S53P4 composition. *Journal of Non-Crystalline Solids*, 498:204–215, 2018.

[36] Aleksandra Wajda, Wolfgang H Goldmann, Rainer Detsch, Aldo R Boccaccini, and Maciej Sitarz. Influence of zinc ions on structure, bioactivity, biocompatibility and antibacterial potential of melt-derived and gel-derived glasses from CaO-SiO2 system. *Journal of Non-Crystalline Solids*, 511:86–99, 2019.