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Degradation study on ternary zinc magnesium phosphate glasses

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Abstract Glasses with composition $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$ ($x = 5$, 8, 10, 13, 15, 18, and 20 mol.%) have been successfully prepared by the melt-quenching technique. Degradation study has been carried out by means of measuring their chemical durability against buffer solutions with initial pH values of 4.01, 7.00, and 10.01 at an ambient temperature for up to 30 days. The dissolution rate (D_R) was obtained by calculating the measured weight loss of the glasses per unit surface area per unit immersion time. The results show that the glasses have better corrosion resistance in basic solution. It was also found that the weight loss is related to the MgO concentration with lower P_2O_5 concentration exhibiting greater corrosion resistance irrespective of acidic, neutral, or basic solutions as immersion liquid. All the sample surfaces and edges were corroded and the solutions experienced a decrease in pH values during the duration of the corrosion test.

Introduction

Phosphate glasses exhibit superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures, and high ultra-violet and far infrared transmissions [1], but their relatively poor chemical durability limits their practical application. However, phosphate-based glasses have been described as the "Third Generation" of biomaterials which offer great potential for degradable temporary scaffolds for the regeneration of hard and soft tissue and would eventually be replaced by natural tissue [2]. The soluble properties of phosphate-based glass eliminate the need of removal surgery, and the breakdown products should not elicit an inflammatory response. The degradation rates can be varied from hours to several weeks even years by changing the glass composition. If the biomaterial is too soluble, it will be resorbed by passive dissolution in the physiologic fluids without giving rise to tissue remodeling. In contrast, active resorption, where cells play a leading role, can occur in less soluble biomaterials, involving them in a process more similar to the biological or natural bone turnover [3]. Since phosphate glasses are structural versatile to accept several cation and/or anion exchanges and this allow the glasses to be physically and compositionally tailored [4] to control their dissolution rate according the desired end application. Hence, knowledge of chemical durability is becoming more important and is a critical requirement as phosphate-based glass materials are either in use or proposed for use as biomaterials.

Pure vitreous pentoxide (P_2O_5) is chemically unstable with regard to hydrolysis of the P–O–P bonding by atmospheric moisture. The addition of metal oxides improves the phosphate glass stability because $P–O–M^+$ (where $M =$ metal cation) bond is generally more stable toward atmospheric hydrolysis or solution attack [5–7]. This has led to the incorporation of oxide like ZnO [8], MgO [9, 10], CaO [2], TiO_2 [7, 11], Fe_2O_3 [12–14], etc. into phosphate glassy network. In addition, trace amounts of Si^{4+}, Sr^{2+}, Mg^{2+}, and Zn^{2+} ions were reported to enhance bone formation [15–18]. Mg^{2+} ion concentration in body has been reported to influence bone strength [17], while zinc is an essential element in bone formation and mineralization [19–21]. Hence, it is of interest to investigate the chemical durability of the simultaneous admixture of MgO and ZnO into the phosphate compositions since there is no any

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literature reported on this glass system and properties. The purpose of the present work was to investigate the chemical durability of zinc oxide magnesium oxide phosphate glass system in acidic, neutral, and basic pH solutions and to elucidate the role undertaken by magnesium ions within the phosphate network.

Materials and methods

This section describes the synthesis of $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$ ($x = 5, 8, 10, 13, 15, 18$, and 20 mol.%) by melt quenching method that have been reported elsewhere [22]. The X-ray diffraction analysis for each glass samples was carried out similarly as reported elsewhere [23]. The samples were finely polished, cleaned in acetone, dried at 110 °C for 1 h, cooled in a desiccator, and weighed with a AND GF-300 electronic balance. The surface area of the glass disks was calculated from the dimensions obtained via Mitutoyo Digimatic Micrometer. After measuring the dimensions, the glass samples were immersed in 10 mL buffer solution and kept at room temperature.

The chemical durability of each glass was determined from the dissolution rate (D_R) in buffer solutions for 30 days. The initial pH of the buffer solutions (Metler Toledo, Switzerland) were 4.01, 7.00, and 10.01, respectively. At various points in time ($\approx$1.5 days intervals), the samples were removed from their respective container, re-cleaned with acetone, re-dried in an oven at 110 °C for 1 h, and reweighed. The weighing accuracy for the glass before and after corrosion was ±0.001 g. The dissolution rate (D_R) for each sample was calculated from the measured weight loss, ΔW (g), sample surface area, A (cm^2), and the immersion time (min), using the relation $D_R = \frac{\Delta W}{(A \cdot t)}$. The ratio of the sample surface area to buffer solution volume was in range of 0.24 to 0.43 cm^{-1}. The pH measurements were taken at every $\approx$1.5 days using a pH-meter S20 (Metler Toledo, Switzerland) with an attached glass combination pH electrode (LE438, Mettler Toledo, Switzerland). The pH electrode was calibrated using pH calibration standards solution (Rainbow Pack pH Buffer Solutions, Switzerland).

Ion release measurement was carried out after 30 days. Each sample solution was filtered, and concentrations of Zn^{2+}, Mg^{2+}, and PO_4^{3-} were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 2000DV). A stock solution containing 1000 mg/L of each element (MERCK, Germany) was used in preparing calibration standards. The calibration solutions were prepared from the stock solution using distilled water immediately before analysis. Correction of data is made by subtracting the normalized analysis on accompanying blank solutions. Chromeleon software (version 6.0) was used for data analysis.

Results and discussion

Dissolution rate

Figure 1 shows a typical X-ray diffraction pattern of the $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$ glassy system. It consists of a broad diffraction halo in the X-ray diffraction pattern which is typical of amorphous structures. The dissolution rate (D_R) of each glass as measured from the weight loss in buffered solutions with initial pH 4.01, 7.00, and 10.01 at an ambient temperature up to 30 days is shown in Fig. 2a–c, respectively. The rate of water absorption is subjected to the hygroscopicity of the hydrolysis product of the glass [24]. For the glass system in pH 4.01, the dissolution rate gradually decreases in the first few days, while in pH 7.00 and 10.01 reverse trends is observed. Such differences in the pH dependency of the studied glass system are suggested to reflect differences in the ability of the hydrolysis process. Further in longer immersion time, the dissolution rate finally reaches an almost constant as observed in all immersion solutions.

The dissolution rates of the glasses also changes depending on the MgO concentration. As the MgO concentration increases, the chemical durability increases. Such dependency may due to the structural alteration of the glasses, implying the generation of stronger glassy matrix that exhibit lower rates of attack by aqueous solutions. The di- or polyvalent modifying cations can provide ionic cross linking between non-bridging oxygen atoms of two phosphate chains and increase the bond strength and chemical durability of the glasses [25]. The improved chemical durability is attributed to the replacement of the easily hydrated P–O–P bonds in the glass by more hydration

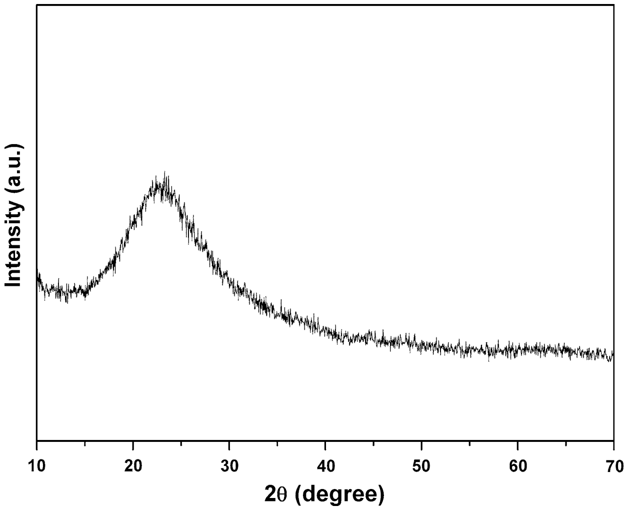

Fig. 1 X-ray diffraction pattern of as prepared $(ZnO)_{30}(MgO)_{20}(P_2O_5)_{50}$ glass representing $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$ ($5 \leq x \leq 20$) glasses

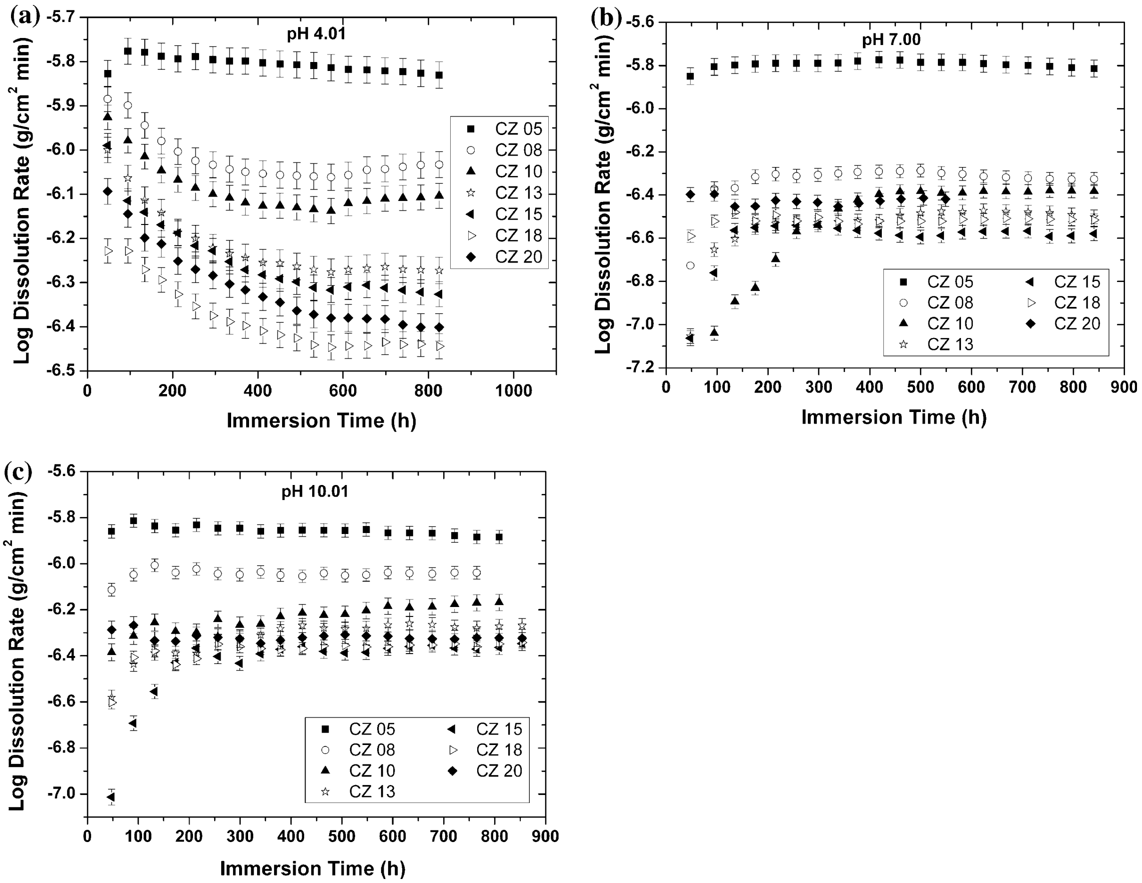

Fig. 2 Effect of increasing MgO content on dissolution rate in solution **a** pH 4.01, **b** pH 7.00, and **c** pH 10.01 at ambient temperature as a function of immersion time

resistance P–O–Mg bonds. As the MgO concentration in the glass increases, the number of P–O–Mg bonds also increases. This explanation is in line with the results of the density and the calculated molar volume of the glasses (tabulated in Table 1) which clearly indicates network expansion on account of participating magnesium ions in the glassy matrix and increase the network connectivity. Such asymmetric bridging oxygen formation leads to a length shortening of the phosphate chains and strengthen the cross-linking between the shorter phosphate chains in the glass structure [26]. Moreover, Mg^{2+} has higher polarizing power (estimated from the ratio of its charge and ionic radius) which causes oxygen attached to it to have a lower basicity, i.e., a lower concentration of negative charge. It therefore serves to reduce its attraction to the positive ends, namely H^+ ions, of H_2O molecules [27]. Hence, the prospect attack of H^+ ions to P–O bonds of P–O–Mg linkages decreases.

Navarro et al. [3] reported that their dissolution rate of phosphate glasses in deionized water was in the range of 1.77×10^{-5} to 2.18×10^{-6} g cm^{-2} h^{-1} which is comparable to the present dissolution rate results on neutral and basic solutions. They also claimed that those soluble glasses have shown potential for use in bone generation. The approximate minimum dissolution rates that are required for osteoblast cell adhesion and proliferation have been measured and were found to be equaled to 1.7×10^{-5} g cm^{-2} h^{-1} [28] and 3×10^{-6} g cm^{-2} h^{-1} [29, 30], respectively. Their results further confirmed the suitability of the present glass system for this purpose.

pH measurement

Figure 3 shows the pH change with time for the studied glass system in buffer solutions with pH 4.01, 7.00, and 10.01. In Fig. 3a, most of the glasses show an increase in their pH values from the starting value of 4.01 before reaching a maximum and declining. It should be noted that the glass with the lowest solubility attains the highest pH value. The initial increase in pH during the corrosion test in the acidic solutions is most likely due to the protonation of the phosphate anion in the solution. As the phosphate network undergoes hydration reaction, the negatively charged oxygen atoms attract hydrogen and formed P–O–H bond. Such reaction effectively removed some amount of hydrogen from the solution and resulting in increment of pH value

Table 1 Composition, density, and molar volume of $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$

Sample code	Composition (mol.%)			Density, ρ ($\pm$0.001 g cm^{-3})	Molar volume, V_m ($\pm$0.001 cm^3 mol^{-1})
	ZnO	MgO	P_2O_5		
CZ 05	30	5	65	3.228	36.768
CZ 08	30	8	62	3.118	37.008
CZ 10	30	10	60	3.045	37.309
CZ 13	30	13	57	2.937	37.643
CZ 15	30	15	55	2.905	37.358
CZ 18	30	18	52	2.815	37.469
CZ 20	30	20	50	2.712	38.143

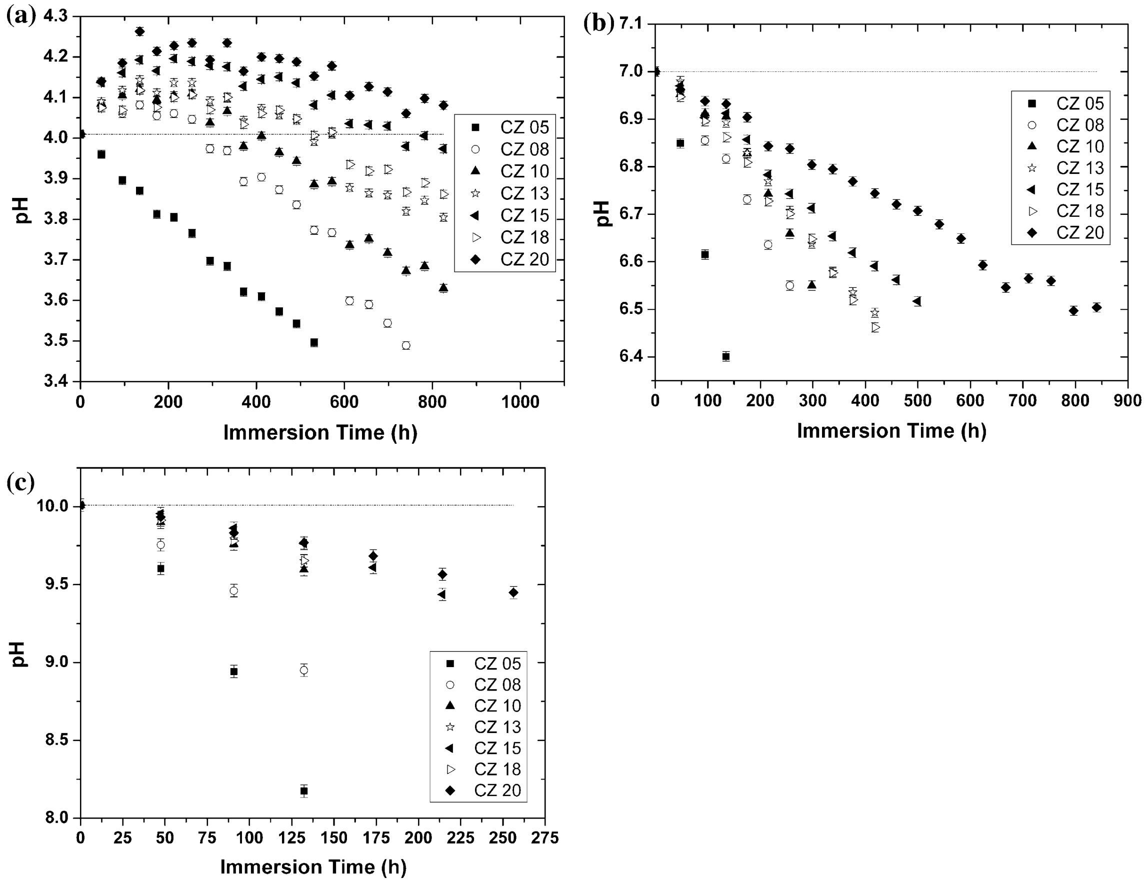

Fig. 3 **a**–**c** The pH values of the buffer solutions at ambient temperature as a function of time. Initial pH of immersion solutions is shown by the *dotted line*

[31]. The pH values of the other two buffer solutions in Fig. 3b and c show a steady decrease with time and this support the dissolution process in the present study.

In general, as can be seen in Fig. 3a–c, the pH value decreases as a function of time. The reduction in pH of all immersion solutions is due to the dissolution of phosphate species from these glasses and the subsequent formation of phosphoric acid [32]. This decrease in pH is consistent with the larger D_R values. The pH values of the immersion solutions at the conclusion of the 30 days corrosion test are observed to depend on the glass composition. The lower pH values were expected for the higher phosphate containing compositions. This is due to the gradual breakdown of the higher phosphate containing compositions probably releasing HPO_4 and PO_4^{3-} ions into the solution thus increasing the acidity of the solution [2]. As the strength of the network structural is enhanced, the solubility of the glass decreases which leads to the reduction of ion levels in the solution. Hence there is discernible pH difference between the different glass compositions.

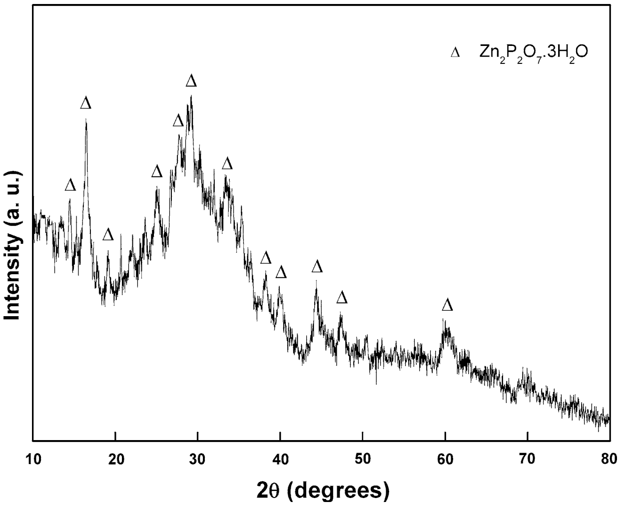

Fig. 4 XRD pattern of white product precipitated in the buffer solution at room temperature

Further evidence of the relative chemical durability of these glasses was apparent from the visual appearance of the external surface of the samples. After the corrosion test, all the glass samples lost their original appearance, and their external surfaces were rough and pitted. The samples with lower MgO concentration were clearly more heavily corroded. In addition, the water absorption and hydrolysis reactions of the glass lead to the formation of white-colored crystalline species which were found in the solutions. Figure 4 shows the XRD pattern of the white product and is identified as $Zn_2P_2O_7 \cdot 3H_2O$. This product may be produced via the hydrolysis mechanism as below:

$$\begin{aligned} &ZnHPO_4(aq) + ZnH_2P_2O_7(aq) + 3H_2O(aq) \\ &\quad \rightarrow H_3PO_4(aq) + Zn_2P_2O_7 \cdot 3H_2O \downarrow . \end{aligned}$$

Ion released measurements

All ions in a glass structure generally tend to leach out of the glass surface when reacted in an aqueous solution. The ion leaching concentration strongly depends on the glass composition and the pH of the aqueous solution. The ratio of surface area of the studied samples (*A*) to the volume of the reacting solution (*V*) was not considered.

Since zinc diphosphate trihydrate formed on the glass surface, Zn^{2+} ions must be supplied from the glass by Zn^{2+} ion leaching. It is believed that the Zn^{2+} ions leach out first and leave a route for Mg^{2+} ion leaching after hydrolysis reaction. As observed in Table 2, the Zn^{2+} and Mg^{2+} ions in the acidic buffer solution with pH 4.01 leach out of the glasses compared to the neutral and basic buffer solutions. Hence, it can be concluded that the ion exchange between Zn^{2+} and H^+ ions under an acidic condition is more active compared to neutral and basic conditions. In solution with pH 7.00, the Zn^{2+} and Mg^{2+} ions leaching are the lowest which may be due to the slowing down of Zn^{2+} ion leaching from the glass surface in neutral solution. Table 2 also shows that there is a correlation observed between the pH values and $PO_4{}^{3-}$ ion release. The breakdown of more $PO_4{}^{3-}$ groups into the solution resulted in a more acidic pH value being obtained. From all the compositions investigated, the amount of Zn^{2+}, Mg^{2+}, and $PO_4{}^{3-}$ ions leaching decreases as a function of MgO concentration indicating higher chemical durability of the glass against aqueous attack irrespective of pH of the immersion solutions.

Table 2 Concentrations of ions leaching in the buffer solutions after corrosion test on $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$ of glasses

Sample code	pH 4.01	pH 7.00	pH 10.01
Zn^{2+} ion concentration (mg/L)			
CZ 05	3222.0	138.8	742.2
CZ 08	1965.1	116.3	211.8
CZ 10	1210.0	194.5	219.3
CZ 13	821.9	108.4	90.9
CZ 15	567.2	125.0	58.6
CZ 18	739.9	59.3	38.0
CZ 20	428.6	55.7	38.9
Mg^{2+} ion concentration (mg/L)			
CZ 05	468.8	246.7	255.8
CZ 08	444.7	240.4	303.5
CZ 10	320.6	193.5	214.0
CZ 13	299.5	208.3	287.8
CZ 15	320.1	206.9	252.2
CZ 18	282.4	253.2	285.9
CZ 20	378.7	175.5	235.7
$(PO_4)^{3-}$ ion concentration (mg/L)			
CZ 05	14607.0	39081.0	16397.0
CZ 08	9667.0	18508.0	10208.0
CZ 10	6496.0	17043.0	7005.0
CZ 13	4506.0	13798.0	7158.3
CZ 15	3771.0	13068.0	5385.0
CZ 18	4217.0	13730.0	6619.5
CZ 20	3383.0	7109.0	5293.0

Conclusions

The degradation of zinc magnesium phosphate glasses in acidic, neutral, and basic solutions has been investigated. The glassy network of these glasses becomes stronger with increasing MgO concentration. The improved chemical durability with increasing MgO concentration is attributed to the easily hydrated P–O–P bonds joining the PO_4 tetrahedra that are being replaced by the more chemically resistance P–O–Mg bonds. The stronger asymmetric bridging oxygen leads to enhanced chemical durability of the glasses regardless of the pH value of the immersion liquid.

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References

1. Mogus-Milankovic A, Licina V, Reis ST, Day DE (2007) J Non-Cryst Solids 353:2659
2. Ahmed I, Lewis M, Olsen I, Knowles JC (2004) Biomaterials 25:491
3. Navarro M, Ginebra M-P, Clément J, Martínez S, Avila G, Planell JA (2003) J Am Ceram Soc 86:1345
4. Desirena H, Schulzgen A, Sabet S, Ramos-Ortiz G, de la Rosa E, Peyghambarian N (2009) Opt Mater 31:784
5. Bae BS, Weinberg MC (1991) J Am Ceram Soc 74:3039
6. Shah KV, Goswami M, Manikandans S, Shrikhande VK, Kothiyal GP (2009) Bull Mater Sci 32:329
7. Monem AS, ElBatal HA, Khalil EMA, Azooz MA, Hamdy YM (2008) J Mater Sci Mater Med 19:1097
8. Takebe H, Baba Y, Kuwabara M (2006) J Non-Cryst Solids 352:3088
9. Franks K, Salih V, Knowles JC, Olsen I (2002) J Mater Sci Mater Med 13:549
10. Ahmed I, Parsons A, Jones A, Walker G, Scotchford C, Rudd C (2010) J Biomater Appl 24:555
11. Rajendran V, Gayathri Devi AV, Azooz M, El-Batal FH (2007) J Non-Cryst Solids 353:77
12. Khan RA, Parsons AJ, Jones IA, Walker GS, Rudd CD (2010) Polym Plastics Technol Eng 49:1265
13. Karabulut M, Yuce B, Bozdogan O, Ertap H, Mammadov GM (2011) J Non-Cryst Solids 357:1455
14. Magdas DA, Cozar O, Chis V, Ardelean I, Vedeanu N (2008) Vib Spectrosc 48:251
15. Ito A, Ojima K, Ichinose H, Tateishi T (2000) J Biomed Mater Res 50:178
16. Marie P, Ammann P, Boivin G, Ray C (2001) Calcif Tissue Int 69:121
17. Okuma T (2001) Nutrition 17:679
18. Xynos ID, Edgar AJ, Buttery LDK, Hench LL, Polak JM (2000) J Biomed Mater Res 276:461
19. Diamond I, Hurley LS (1970) J Nutr 100:325
20. Hall SL, Dimai HP, Farley JR (1999) In Vitro Calcif Tissue Int 64:163
21. Wu X, Itoh N, Taniguchi T, Nakanishi T, Tatsu Y, Yumoto N, Tanaka K (2003) Arch Biochem Biophys 420:114
22. Khor SF, Talib ZA, Daud WM, Sidek HAA, Ng BH (2009) J Non-Cryst Solids 355:2533
23. Sidek HAA, Rosmawati S, Talib ZA, Halimah MK, Daud WM (2009) Am J Appl Sci 6:1489
24. Palavit G, Mercier C, Montagne L, Drache M, Abe Y (1998) J Am Ceram Soc 81:1521
25. Brauer DS, Russel C, Kraft J (2007) J Non-Cryst Solids 353:263
26. Brow RK, Tallant DR, Myers ST, Phifer CC (1995) J Non-Cryst Solids 191:45
27. Marino AE, Arrasmith SR, Gregg LL, Jacobs SD, Chen GR, Duc YJ (2001) J Non-Cryst Solids 289:37
28. Burling LD (2005) PhD thesis, University of Nottingham
29. Bitar M, Salih V, Mudera V, Knowles JC, Lewis MP (2004) Biomaterials 25:2283
30. Parsons AJ, Evans M, Rudd CD, Scotchford CA (2004) J Biomed Mater Res A 71A:283
31. Tischendorf BC (2005) Interaction between water and phosphate glasses. PhD Dissertation, Department of Ceram Engineering, Missouri-Rolla University, Rolla, MO
32. Yu X, Day DE, Long GJ, Brow RK (1997) J Non-Cryst Solids 215:21