Ashdin Publishing
Bioceramics Development and Applications
Vol. 1 (2011), Article ID D110148, 3 pages
doi:10.4303/bda/D110148

Research Article

Ion Releasing Abilities of Phosphate Invert Glasses Containing MgO, CaO or SrO in Tris Buffer Solution

S. Lee, A. Obata, and T. Kasuga

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan
Address correspondence to T. Kasuga, kasuga.toshihiro@nitech.ac.jp

Received 14 January 2010; Accepted 3 February 2010

Abstract CaO-TiO$_2$-P$_2$O$_5$-Na$_2$O invert glasses developed in our group showed bioactivity and good sinterability. In the present work, phosphate invert glasses, in which CaO was substituted with MgO or SrO (PIG-MO, M = Mg, Ca, Sr), were prepared and their ion-releasing behaviors were evaluated. Glass transition temperature (Tg) and crystallization temperature (Tc) were estimated from differential thermal analysis. (Tc – Tg)/Tg value, which indicates glassification of the glass, of PIG-MgO was higher in comparison with those of the other glasses. Laser Raman spectroscopic analysis indicated that peaks due to $P_2O_7{}^{4-}$ group in the spectrum of PIG-MgO were smaller than those in the spectra of PIG-CaO and PIG-SrO. The structure of $PO_4{}^{3-}$-M^{2+}-$PO_4{}^{3-}$ was expected to form easily, resulting in the good glassification of PIG-MgO. The ion amounts dissolved from PIG-MgO containing a large amount of $PO_4{}^{3-}$ group were $2 \sim 3$ times larger than those of the other glasses.

Keywords phosphate glass; magnesium; calcium; strontium; ion release; biomaterial

1 Introduction

CaO-TiO$_2$-P$_2$O$_5$-Na$_2$O invert glasses (Phosphate Invert Glasses, denoted by PIGs), which contain ortho- and pyrophosphate groups, were successfully prepared by a conventional melting method in our group [5]. Powders of the glasses have good sinterability when heated at 850 °C [4]. Hydroxyapatite deposits on the glass and glass-ceramic surfaces after soaking in simulated body fluid (SBF) [4,6]. The glass-ceramics was successfully coated on a Ti-29Nb-13Ta-4.6Zr alloy [7,10] and then expected to be applicable to coating for artificial implant materials.

Trace amounts of Si^{4+}, Sr^{2+}, Mg^{2+}, and Zn^{2+} ions were reported to enhance bone formation [3,8,11,17]. We have investigated in PIGs which release these ions. Mg^{2+} and Sr^{2+} ions can be easily substituted with Ca^{2+} ions in PIG. Mg^{2+} ion concentration in body has been reported to influence bone strength [11]. Sr^{2+} ion has been reported to inhibit bone resorption by osteoclasts and enhance bone formation by osteoblasts [8]. Wu et al. developed calcium-magnesium phosphate cement. The calcium-magnesium phosphate cement induced higher proliferation of human osteosarcoma MG63 cells in comparison with calcium phosphate cement [16]. Qie et al. prepared calcium polyphosphate substituted with strontium. The proliferation and alkaline phosphatase (ALP) expression of osteoblast-like cell line (ROS17/2.8) were higher on the calcium polyphosphate substituted with < 20 mol% strontium than on an unsubstituted one [13].

The present work was a fundamental study for developing new types of glasses with Mg^{2+}, Ca^{2+} and Sr^{2+} ion releasability. PIG, in which CaO was substituted with MgO or SrO, was prepared by a conventional melt-quenching method and evaluated in their solubilities in Tris buffer solution (pH 7.40), assuming to the body system. The glass structures and their glassification were discussed.

2 Materials and methods

$60MO{\cdot}30P_2O_5{\cdot}7Na_2O{\cdot}3TiO_2$ (mol%, M = Mg, Ca, Sr, nominal composition, denoted by PIG-MO) were prepared. Glass batches were prepared using MgO (99.5%), CaCO$_3$ (99.5%), SrCO$_3$ (98%), H$_3$PO$_4$ (85% liquid), Na$_2$CO$_3$ (99.5%), and TiO$_2$ (99.5%). All regeagents were purchased from Kishida Chemical Co. The reagents were mixed with distilled water to make a slurry, and then dried at 140 °C overnight. The resulting sample was melted at 1400 °C for 30 min and then quenched on a stainless steel, resulting in the formation of the glass. Glass transition temperature (Tg) and crystallization temperature (Tc) of the resulting glasses were estimated from differential thermal analysis (DTA, Rigaku Thermo plus, TG8120), which was performed until 1000 °C at a heating rate of 5 °C/min. Glass structure was examined by laser Raman spectroscopy (LRS, JASCO, NRS-2000, 514.5 nm).

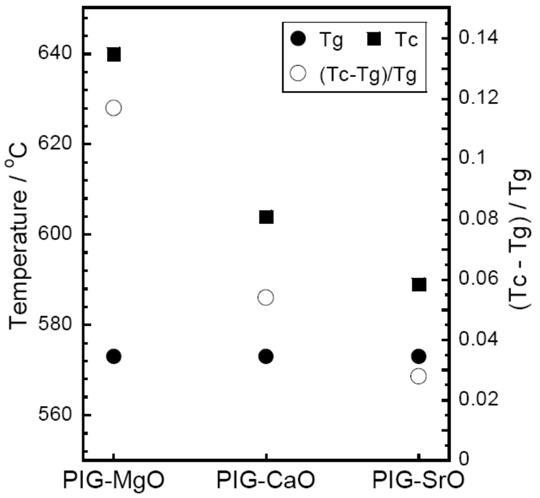


Figure 1: Tg, Tc and (Tc – Tg)/Tg values of the glasses.

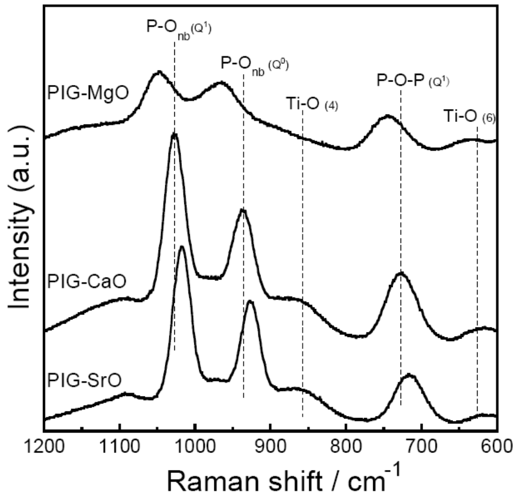


Figure 2: Laser Raman spectra of the glasses.

The glasses were pulverized into 125 ~ 300 μm in size. Tris buffer solution was prepared using 6.118 g of Trishydroxymethylaminomethene ($NH_2C(CH_2OH)_3$, Kishida Chemical Co.) and 1 liter of distilled water and its pH was adjusted to 7.40 at 37 °C using hydrochloric acid. 15 mg of the glass powders were soaked in 15 mL of Tris buffer solution at 37 °C for 1 week. The amounts of the ions dissolved from the glasses were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu, ICPS-7000).

3 Results and discussion

Figure 1 shows Tg, Tc, and (Tc – Tg)/Tg, which indicates a degree of glassification [12]. The (Tc – Tg)/Tg value of PIG-MgO is twice larger than that of PIG-CaO, and the value of PIG-SrO is half of that of PIG-CaO. PIG-MgO is suggested to show good glassification due to its larger (Tc – Tg)/Tg value than those of the others.

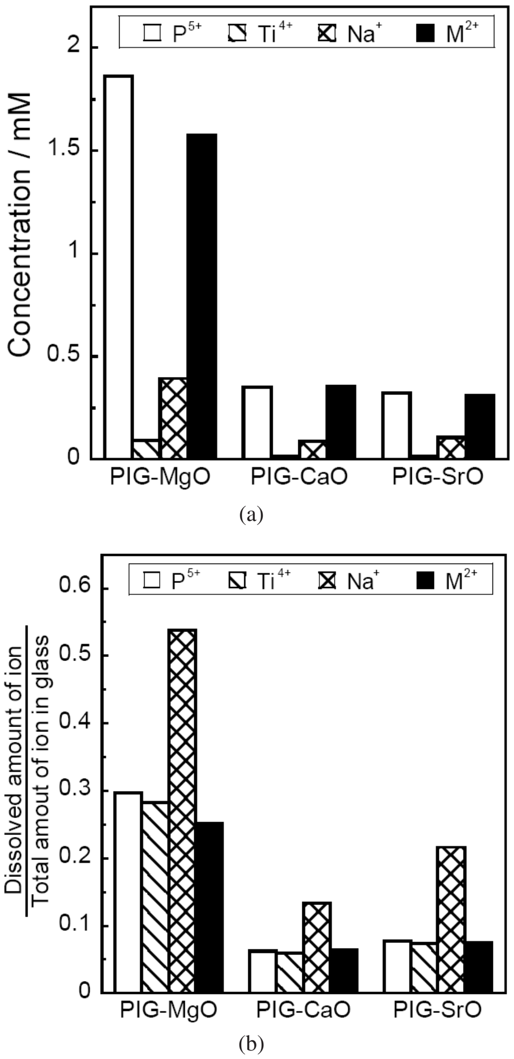
Figure 2 shows laser Raman spectra of the glasses. The peaks matching to phosphate groups are as follows; 1040 cm^{-1}: P-O stretching due to non-bridging oxygen Q^1 species, 950 cm^{-1}: P-O stretching due to non-bridging oxygen Q^0 species and 740 cm^{-1}: P-O-P stretching due to bridging oxygen Q^1 species [1]. Q^0 and Q^1 indicate orthophosphate (PO_4^{3-}) and pyrophosphate ($P_2O_7^{4-}$) groups, respectively. The peaks matching to Ti-O polyhedra are as follows; 880 cm^{-1}: TiO_4 tetrahedra and 650 cm^{-1}: TiO_6 octahedra [15]. The peaks due to Q^0, Q^1 and TiO_6 appeared in the all of the spectra. The peaks due to TiO_4 appeared in PIG-CaO and PIG-SrO. The pyrophosphate (Q^1) peaks of PIG-MgO was smaller than those of the other glasses. All peaks red-shifted with increasing atomic number of M (Mg, Ca, Sr) in the glasses. Dietzel proposed the field strength that is the simplified Coulomb's force in oxides.

$$F = \frac{Z}{a^2} \quad \left(\text{valance/Å}^2\right).$$

F is field strength, Z is cation valance and a is distance between cation and anion. The field strength of Mg^{2+}, Ca^{2+}, and Sr^{2+} ions are 0.53 (4-fold coordination) or 0.46 (6-fold coordination), 0.33, and 0.28 valance/$Å^2$, respectively [2]. Nelson et al. reported that Raman peaks of phosphate groups in alkaline earth metal containing phosphate glasses red-shifted with increasing the atomic number of the metals [9]. As the atomic numbers of the metals increase, their field strengths decrease. This causes attributes to the increase in the angle of P-O-P bonds in PO_4 tetrahedra. The Raman peaks red-shifted with the increase in O-P-O angle, due to decrease in its bonding energy [14].

Figure 3(a) shows the ion concentration in Tris buffer solution after soaking the glass powders for 1 week, and Figure 3(b) shows the ratios of the dissolved ion-amount to the total one in the glasses. The ion amounts dissolved from PIG-MgO were about 2 ~ 3 times larger than those from the other glasses.

The field strength of Mg^{2+} ion is larger than those of Ca^{2+} and Sr^{2+} ions and Mg-O bonding strength is larger than those of Ca-O and Sr-O. LRS analysis showed that pyrophosphate group (Q^1) peaks in the spectrum of PIG-MgO were smaller in comparison with those of the others. This means PIG-MgO contains a larger amount of orthophosphate group (Q^0) than PIG-CaO and PIG-SrO. The structure of PO_4^{3-}-M^{2+}-PO_4^{3-} is suggested to form more easily in PIG-MgO in comparison with the other glasses. This may cause the good glassification of PIG-MgO, as shown in Figure 1. The (Tc – Tg)/Tg value of



(a)

(b)

Figure 3: Ion amounts dissolved from the glasses in Tris buffer solution after soaking for 1 week. (a) Concentration of ions in Tris buffer solution, and (b) ratio of dissolved ions against their total amounts in the glasses.

PIG-MgO is high, while the glass contains a larger amount of Q^0 than the others. In the case of PIG-CaO and PIG-SrO, pyrophosphate groups (Q^1) formed predominantly, since the field strengths of Ca^{2+} and Sr^{2+} are smaller than that of Mg^{2+}.

The bonding strength of $P_2O_7{}^{4-}$-M^{2+} may be larger than that of $PO_4{}^{3-}$-Mg^{2+}. The dissolution behavior of PIG-MgO is suggested to be attributed to a large amount of orthophosphate group in the glass.

4 Conclusions

MO-TiO_2-P_2O_5-Na_2O invert glasses (M = Mg, Ca, Sr) were prepared and evaluated in their glass structures and ion-releasing abilities in Tris buffer solution. Although PIG-MgO contained a larger amount of orthophosphate group than the other glasses, it showed good glassification due to the high field strength of Mg^{2+}. On the other hand, PIG-MgO showed lower chemical durability due to a large amount of orthophosphate group. M^{2+} ions in the phosphate invert glasses play an important role in their glassification and ion-releasing.

References

[1] R. K. Brow, D. R. Tallant, S. T. Myers, and C. C. Phifer, *The short-range structure of zinc polyphosphate glass*, J Non Cryst Solids, 191 (1995), 45–55.

[2] A. Dietzel, *Die kationenfeldstärken und ihre beziehungen zu entglasungsvorgängen, zur verbindungsbildung und zu den schmelzpunkten von silicaten*, Ztchr Elektrochem, 48 (1942), 9–23.

[3] A. Ito, K. Ojima, H. Ichinose, and T. Tateishi, *Preparation, solubility, and cytocompatibility of zinc-releasing calcium phosphate ceramics*, J Biomed Mater Res, 50 (2000), 178–183.

[4] T. Kasuga and Y. Abe, *Novel calcium phosphate ceramics prepared by powder sintering and crystallization of glasses in the pyrophosphate region*, J Mater Res, 13 (1998), 3357–3360.

[5] ———, *Calcium phosphate invert glasses with soda and titania*, J Non Cryst Solids, 243 (1999), 70–74.

[6] T. Kasuga, Y. Hosoi, M. Nogami, and M. Niinomi, *Apatite formation on calcium phosphate invert glasses in simulated body fluid*, J Am Ceram Soc, 84 (2001), 450–452.

[7] T. Kasuga, M. Nogami, M. Niinomi, and T. Hattori, *Bioactive calcium phosphate invert glass-ceramic coating on β-type Ti–29Nb–13Ta–4.6Zr alloy*, Biomaterials, 24 (2003), 283–290.

[8] P. Marie, P. Ammann, G. Boivin, and C. Ray, *Mechanisms of action and therapeutic potential of strontium in bone*, Calcif Tissue Int, 69 (2001), 121–129.

[9] B. N. Nelson and G. J. Exarhos, *Vibrational spectroscopy of cation-site interactions in phosphate glasses*, J Chem Phys, 71 (1979), 2739–2747.

[10] M. Niinomi, *Mechanical properties of biomedical titanium alloys*, Mater Sci Eng A, 243 (1998), 231–236.

[11] T. Okuma, *Magnesium and bone strength*, Nutrition, 17 (2001), 679–680.

[12] M. Ouchetto, B. Elouadi, and S. Parke, *Study of lanthanide zinc phosphate glasses by differential thermal analysis*, Phys Chem Glasses, 32 (1991), 22–28.

[13] K. Qiu, X. J. Zhao, C. X. Wan, C. S. Zhao, and Y. W. Chen, *Effect of strontium ions on the growth of ROS17/2.8 cells on porous calcium polyphosphate scaffolds*, Biomaterials, 27 (2006), 1277–1286.

[14] G. B. Rouse Jr., P. J. Miller, and W. M. Risen Jr., *Mixed alkali glass spectra and structure*, J Non Cryst Solids, 28 (1978), 193–207.

[15] S. Sakka, F. Miyaji, and F. Fukumi, *Structure of binary K_2O—TiO_2 and Cs_2O—TiO_2 glasses*, J Non Cryst Solids, 112 (1989), 64–68.

[16] F. Wu, J. Wei, H. Guo, F. Chen, H. Hong, and C. Liu, *Self-setting bioactive calciummagnesium phosphate cement with high strength and degradability for bone regeneration*, Acta Biomater, 4 (2008), 1873–1884.

[17] I. D. Xynos, A. J. Edgar, L. D. K. Buttery, L. L. Hench, and J. M. Polak, *Ionic products of bioactive glass dissolution increase proliferation of human osteoblasts and induce insulin-like growth factor II mRNA expression and protein synthesis*, J Biomed Mater Res, 276 (2000), 461–465.