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Fabrication of P_2O_5–CaO–Na_2O glasses doped with magnesium oxide for artificial bone applications

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Abstract

Effects of MgO doping on properties of P_2O_5–CaO–Na_2O glass system were investigated. The glass samples were prepared by conventional glass melting technique at 1000 °C for 1 h. Thermal parameter of each glass sample were studied by differential thermal analysis (DTA). The glass samples were annealed at crystallization temperature to form glass ceramics. The glass ceramics were investigated in terms of phase formations by XRD, microstructure by SEM and in vitro bioactivity. The phases formed in all glass ceramics are calcium phosphate ($Ca_2P_2O_7$ file no. 09-0346), sodium phosphate ($NaPO_3$ file no. 11-0650) and sodium calcium phosphate ($Na_{1.8}Ca_{1.1}P_6O_{17}$ file no. 47-0863) as detected by XRD. The 5–10 mol% MgO glass ceramics having well separated two crystallization peaks (T_{x1} and T_{x2}) within the temperature range of 557–590 °C contained additional sodium magnesium phosphate ($NaMg(PO_3)_3$ file no. 72-2341). Large porosity was found in all glass ceramics due to free volume and void formation during the crystallized phase. The in vitro study revealed that all glass ceramic samples exhibited apatite cell growth at the surface after immersed in simulated body fluid (SBF) for 7 days. The results suggested that these glass ceramics were appropriate for biomedical application.

Keywords: B. Porosity; C. Thermal properties; D. MgO; E. Biomedical applications

1. Introduction

Bioactive glasses and ceramics, such as hydroxyapatite, β-tricalcium phosphate, 45S5 bioglass®, calcium phosphate glass and A-W glass ceramics are biomaterials, which when implanted into bone defects, form spontaneously a layer of bonelike apatite on the surface that induces chemical integration of bone cells [1–5]. Recently, many researchers have attempted to improve these bioactive materials for bonelike apatite growth capability.

Trace ions, such as Na^+, Mg^{2+}, K^+ and F^- are prevalent in the organic part of bone. It was found that of hydroxyapatite doped with some of these metallic ions had improvement in osteoblast adhesion and the increase in intracellular alkaline phosphates activity [6]. These modified hydroxylapatite also showed excellent cell attachment and cell spreading of a modified human osteoblast (HOB) cells lining on the matrices. Calcium phosphate glasses containing silica, non-silica phosphate glasses and other oxides such as Na_2O, MgO, ZnO, TiO_2, K_2O and Fe_2O_3, [7–9] have also attracted a lot of interest for biomaterial application. Calcium phosphate glasses containing silica, indicated toxicity on mice [10]. However, non-silica calcium phosphate glasses have shown to be non-toxic because of their chemical composition is closely similar to that of natural bone. They also have bioresorbable property that enable these glasses to be dissolved in human fluids, so it can be slowly replaced by regenerated tissue [11–12].

The ternary P_2O_5–CaO–Na_2O glasses are one of the interesting calcium phosphate glass systems without silica group. These glasses can be dissolved in water, simulated body fluid (SBF) and body fluid, which is replaced by regenerated tissue as these glasses have shown good biodegradable and biocompatibility in vitro and in vivo

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tests [5,7,13–16]. In addition, these glass systems were found to exhibit thermal parameters at low temperature, which can be easily melted and casted [13,17,18]. Previous works showed that the P_2O_5–CaO–Na_2O glass with fixed P_2O_5 content of 45 mol% gave a good range of glasses, which are easily processed and good biocompatibility [13,19]. This work, therefore has attempted to modify these glasses by substituting CaO by MgO from 2.5 mol% to 10 mol% with fixed amount of P_2O_5 and Na_2O of 45 mol% and 25 mol%, respectively.

2. Experimental

2.1. Glass preparation

The glasses were prepared using $(NH_4)_2HPO_4$, $CaCO_3$, Na_2CO_3 and $Mg(OH)_2$ as starting materials and the formula used in this study is $45P_2O_5$–$(30-x)$CaO–$25Na_2O$–xMgO where $x=0$, 2.5, 5, 7.5 and 10 mol%. The mixing materials were melted at 1000 °C for 1 h in alumina crucible and the melts were quenched between stainless steel plated in air. The glasses were subsequently examined by differential thermal analysis (DTA: Stanton redcroft DTA model 673-4) using Al_2O_3 as reference.

2.2. Glass ceramic preparation

The glasses were annealed at their corresponding crystalline temperature (T_x) for 5 h with heating and cooling rate of 5 °C/min. Phase formation of the prepared glass ceramics were investigated by X-ray diffraction (XRD: Rigaku Mini Flex II). In vitro bioactivity was assessed in SBF, which was buffered to pH 7.4. The glass ceramic samples were soaked in SBF and indicated for 7 days at 36.5 °C. The microstructures of glass ceramics before and after immersed in SBF were investigated by scanning electron microscopy (SEM: JSM-5910). Energy dispersive X-ray spectroscopy (EDS) was employed for chemical analysis of the glass ceramics after immersed in SBF.

3. Results and discussion

Thermal properties of all glasses examined by DTA are shown in Fig.1. The glass transition temperature (T_g) appeared in the range of 411–417 °C as tabulated in Table 1. The increase of MgO content did not significantly affect the change in T_g. For the dopant of MgO at 0–2.5 mol%, the first and the second peaks of crystallization temperatures (T_{x1} and T_{x2}) overlapped in the range of 525–555 °C. The 5–10 mol% MgO glasses have shown clearer splitting of T_{x1} and T_{x2} in the range of 557–590 °C. This may be attributed to the addition of MgO, which subsequently altered the CaO/P_2O_5 molar ratio of the glass network. As it is known that Ca^{2+} ions form the stronger cross-link of groups than that of Na^+ ions [13,19].

The XRD patterns of the glass ceramics annealed at their corresponding T_{x2} are shown in Fig. 2. The main phase found in all glass ceramics are calcium phosphate ($Ca_2P_2O_7$ file no. 09-0346), sodium phosphate ($NaPO_3$ file no. 11-0650) and sodium calcium phosphate ($Na_{1.8}Ca_{1.1}P_6O_{17}$ file no. 47-0863) phases. Morever the glass ceramic samples with 5–10 mol% MgO contained the additional sodium magnesium phosphate ($NaMg(PO_3)_3$ file no. 72-2341) phase, which may correspond to well split T_{x1} and T_{x2} (Fig. 1) at higher temperatures comparing to that of lower MgO content samples (0–2.5 mol% MgO).

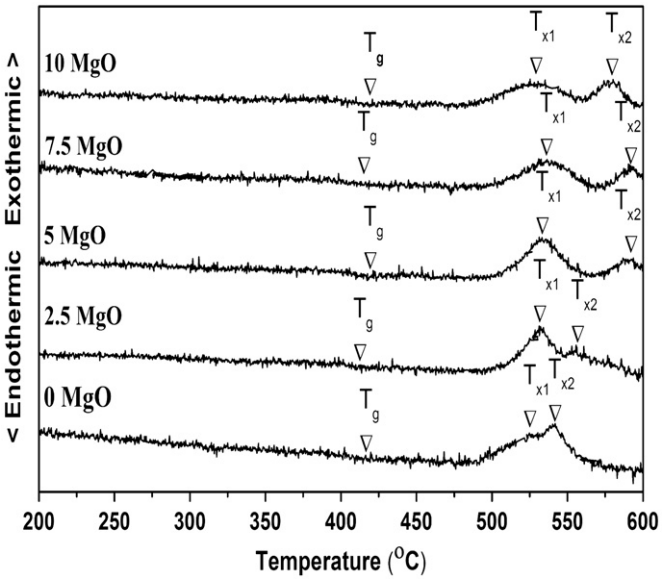

Fig. 1. DTA trace of all glass samples.

Table 1
Codes and thermal parameter of P_2O_5–CaO–Na_2O–MgO glasses.

Code	Thermal parameter (°C)		
	T_g	T_{x1}	T_{x2}
45P30C25N	415	525	541
45P27.5C25N2.5M	411	532	554
45P25C25N5M	417	533	590
45P22.5C25N7.5M	413	534	590
45P20C25N10M	417	527	578

Large pores with the size ranging from 100 nm to 200 nm are illustrated in Fig. 3(a) for undoped sample, which may be due to mass transport of many atoms and ions during crystallization at T_{x2}. This may be in turn beneficial to cell growth as described in previous works [20,21]. Fig. 3(b) and (c) shows the denser structure of the 7.5% doped glass ceramic containing well distributed crystals which were formed similarly in all doped samples after annealing. It may be noted that the MgO doped samples tend to have better mechanical robust than that of the undoped one. However, nano indentation may be needed for precise assumption.

For the in vitro bioactive test the apatite cells were found on the surface of all glass ceramics as shown in SEM microstructures (Fig. 4). The chemical compositions of the

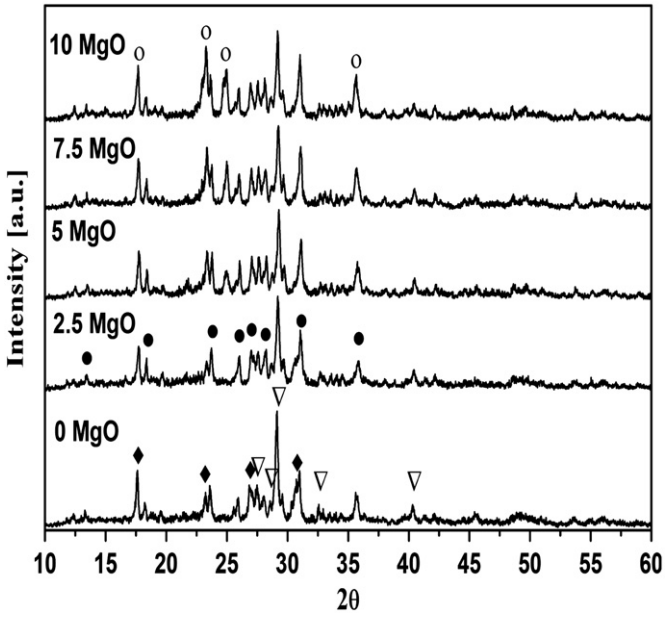

Fig. 2. XRD patterns of the glass ceramics after annealed at their corresponding T_{x2}: $Ca_2P_2O_7$ file no. 09-0346 (▽), $NaPO_3$ file no. 11-0650 (♦), $Na_{1.8}Ca_{1.1}P_6O_{17}$ file no. 47-0863 (●) and $NaMg(PO_3)_3$ file no. 72-2341 (o).

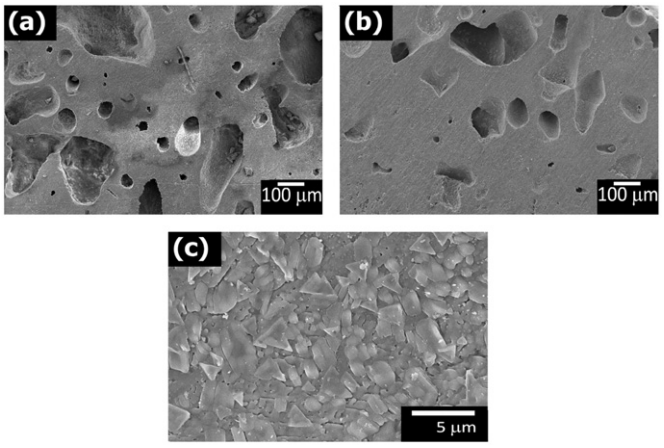

Fig. 3. Microstructures of glass ceramic samples after annealing at T_{x2}: (a) 100 x of undoped sample, (b) 100 × and (c) 5000 × of 7.5% MgO doped sample.

cells were detected by EDX (Fig. 5). On each surface, the formation of individual apatite grains with spherical in shape with diameter in nanosize range are clearly revealed. The typical spectra of apatite cells in 0 mol% MgO sample contains P, Ca, and O atoms while in that of 2.5–10 mol% samples are P, Ca, Na, Mg and O. The apatite formation mechanism in non MgO samples explained by dissolution of Ca^{2+} and Na^+ while for MgO added samples explained by dissolution of Ca^{2+}, Mg^{2+} and Na^+. The results suggested that these glass ceramics were appropriated glass ceramics for biomedical application.

It can be noted that after immersion in SBF solution for 7 days, the glass ceramics surfaces show some degree of

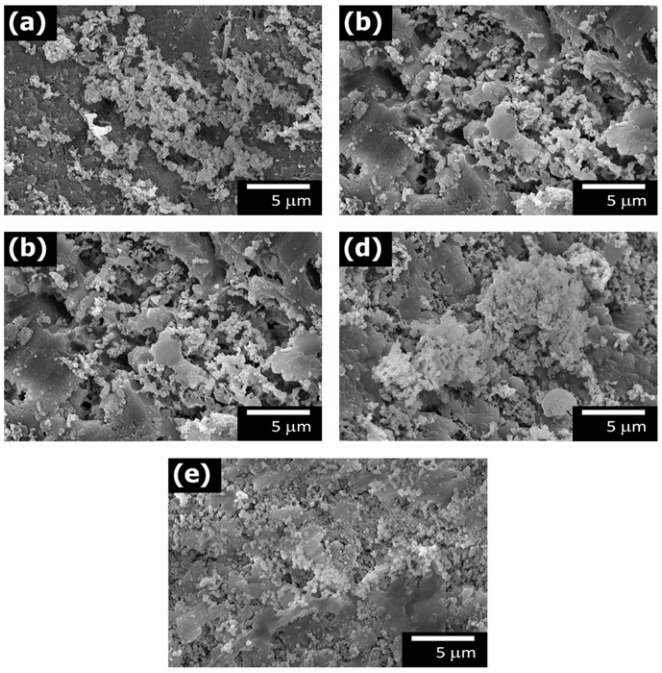

Fig. 4. Microstructures of glass ceramics after immersions in SBF solution for 7 days: (a) 0 mol%, (b) 2.5 mol%, (c) 5 mol%, (d) 7.5 mol% and (e) 10 mol%.

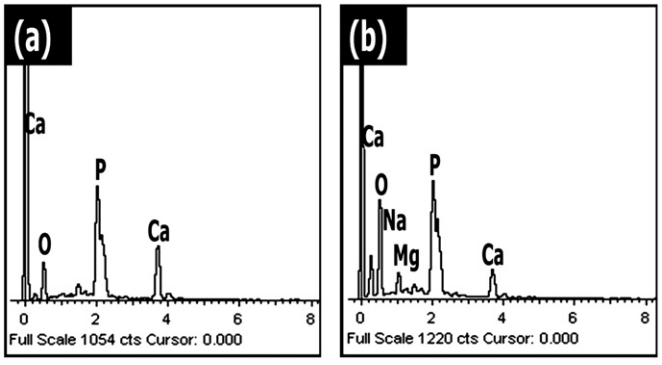

Fig. 5. The EDS spectra of apatite cells on surface of glass ceramics recorded after immersion in SBF solution for 7 days: (a) 0 mol% MgO and (b) 2.5–10 mol%.

wearing out by comparing with the surface of the glass ceramic before immersion in SBF. (Fig. 3(b)). The degree of wearing out was found to increase with increasing MgO content to 5 mol% and decrease with increasing MgO content of more than 5 mol%. This result is consistent with the work done by Frank et al. [22] that the solubility of ions was found to be inhibited when MgO was used to substitute CaO in glass network.

4. Conclusions

The phase found in all glass ceramics are calcium phosphate ($Ca_2P_2O_7$ file no. 09-0346), sodium phosphate ($NaPO_3$ file no. 11-0650) and sodium calcium phosphate

($Na_{1.8}Ca_{1.1}P_6O_{17}$ file no. 47-0863) phases. The dopant of 5–10 mol% MgO resulted in another magnesium phosphate phase, crystallizing at T_{x2}. The glass ceramics contained high because free volume and pores generate during crystal phase formation. For in vitro study, all glass ceramics exhibited apatite cells growth at their surface after immersed in SBF for 7 days. The results suggested that these glass ceramics were appropriated glass ceramics for biomedical application.

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