ELSEVIER

Thermochimica Acta 339 (1999) 103–109

thermochimica acta

www.elsevier.com/locate/tca

A study on thermal properties of β-$Ca(PO_3)_2$ whiskers and on devitrification mechanism of calcium phosphate glass system

Jinn-Shing Lee[a,b,c,*], Chung-King Hsu[a]

[a]*Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC*
[b]*Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taiwan, ROC*
[c]*Chung Shan Institute of Science and Technology, PO Box 90008-15-9, Lung-Tan, Taiwan, ROC*

Received 1 March 1999; received in revised form 18 June 1999; accepted 9 July 1999

Abstract

β-$Ca(PO_3)_2$ whiskers were successfully extracted from crystallized calcium phosphate glasses by leaching with distilled water or aqueous solution of 0.1–0.5 N NaOH. β-$Ca(PO_3)_2$whiskers of aspect ratios (16–400) were obtained from the crystallized glasses with Ca/P molar ratio smaller than 0.4. It is expected that the β-$Ca(PO_3)_2$ whiskers are available for new applications to biomedical fields. In this study, the morphology and the melting point of β-$Ca(PO_3)_2$ whiskers that obtain from the crystallized glasses with different particle size will be investigated.

β-$Ca(PO_3)_2$ whiskers having aspect ratios of (16–400) with diameter of 3–30 μm was found from a crystallized glass with Ca/P molar ratio of 0.25, but the morphology of β-$Ca(PO_3)_2$ whiskers of crystallized glass before leaching are not clear because of the existence of glass phase, so the extraction step is needed for preparation of the β-$Ca(PO_3)_2$ whiskers. The curves of TG and DTA for the resultant powder before extraction step gave a high mass loss percentage (approximation 14%) and melt completely at about 900°C with a broad endothermic peak in DTA curve. But the resultant whiskers that after extraction step gave only 1% mass loss in TG curve and melt completely at 980°C with a sharp endothermic peak.

Keywords: β-$Ca(PO_3)_2$ whiskers; Thermal properties; Low Ca/P molar ratio; Calcium phosphate glass

1. Introduction

Phosphate glasses and its crystallized products have a special interesting in bio-material fields recently [1], and the high-strength β-calcium meta-phosphate fibers for new applications to biomedical fields were also successfully extracted from crystallized products of non-stoichiometric calcium phosphate glass, through a heating process then by leaching with a solution [2]. Although calcium phosphate glass-ceramics posess a high potential in use as bio-substitute materials, such as artificial bones or dental crowns, till now, high-strength and high-toughness bio-materials with low elastic modulus, bio-compatible and not toxic were not reported that the calcium phosphate glasses and glass-ceramics possessed satisfactory properties for biomedical applications.

Griffith found that a melt in the Na_2O–CaO–P_2O_5 system is an advantageous medium for the long polyphosphate fibers to be grown [3], and it is pointed out, however, that straight $Ca(PO_3)_2$ fibers with high aspect

---

[*] Corresponding author. Fax: +886-2-2-7719819
E-mail address: ckhsu@ntut.edu.tw (J.-S. Lee)

PII: S0040-6031(99)00221-X

ratios are good for reinforcement. In general, the mechanical properties of ceramic or polymer materials are effectively improved by introducing some fibers into the bulk materials, It has been reported that the uni-directionally $Ca(PO_3)_2$ glass-ceramics having fiber-reinforced composite crystallized structure was successfully produced by re-heating a calcium meta-phosphate glass rod under a temperature gradient around the glass transition temperature [4,5]. This glass-ceramic composed of crystalline β-$Ca(PO_3)_2$ fibers shows high-bending strength of 400–600 MPa and low Young's modulus of 70–120 GPa; this implies that the β-$Ca(PO_3)_2$ fibers are of high strength and flexibility, in addition, this glass-ceramic exhibits good bio-compatibility therefore, it is expected that β-$Ca(PO_3)_2$ fiber can be used for new composite bio-materials.

In this work, the devitrification phenomenon of calcium phosphate glass with various Ca/P molar ratios were investigated firstly, and the kinetic parameters, such as activation energy parameter that depend on the mechanism and morphology of crystal growth etc., were calculated using non-isothermal DTA techniques. At the same time, the effect of particle size, leaching process of crystallized glass on the morphologies and thermal properties of β-$Ca(PO_3)_2$ were also examined using DTA/TG and using scanning electron microscopy.

2. Experimental

Batches of mixtures with various Ca/P molar ratios (0.25–0.15) were prepared by mixing $Ca(H_2PO_4)_2H_2O$, $CaCO_3$ and H_3PO_4 with ethanol in ball miller for 30 min, the composition of glasses are listed in Table 1. After being dried the powder of mixtures were melt in a Pt crucible in an electrical furnace at 1350°C for 2 h, melted glasses are poured into a preheated graphite mold (about 280°C), and cooled to room temperature in order to harden into a glass block. The powdered samples were prepared by crashing the glass blocks in a stainless steel mortar and pestle, then sieved in order to obtain a coarse powder between 30 and 50 mesh and very fine (-325 mesh) particles. DTA curves of each approximately 10 mg of fine and coarse glass powders at different heating rates (2–20°C min^{-1}), under static air atmosphere were recorded. A Rigaku-Denki thermoanalyzer (model 8121) was used, and powder α-Al_2O_3 was used as reference material. The crystalline phases of the resultant products were also identified by Rigaku-Denki X-ray diffraction (XRD). The surface morphologies of resultant products were observed using JEOL JSM-6300 scanning electron microscopy.

3. Results and discussions

Thermal analysis has been widely used to study the kinetics of chemical reaction [6], as the reaction proceeded, the heat of reaction is evolved (or absorbed) and an exothermic (or endothermic) peak appears on the DTA curve. The non-isothermal devitrification is well described by the well know equation [7,8]

$$\ln(\beta^n/T_p^2) = -mE_c/RT_p + \text{const.} \tag{1}$$

Eq. (1) which is the modified Kissinger equation, has been widely used in the kinetic study of the non-

Table 1
Compositions of raw material for preparation of calcium phosphate glasses

No.	Ca/P molar ratio	$Ca(H_2PO_4)_2\ 2H_2O$ (g)	$CaCO_3$ (g)	H_3PO_4 (ml)
1	0.65	40	6.3538	0.00
2	0.60	40	4.7654	0.00
3	0.55	40	3.1769	0.00
4	0.50	40	1.5885	0.00
5	0.45	40	0.0000	2.40
6	0.40	40	0.0000	5.41
7	0.35	40	0.0000	9.27
8	0.30	40	0.0000	14.43
9	0.25	40	0.0000	21.64

Table 2
Kinetic parameters of calcium phosphate glasses, evaluated by non-isothermal DTA technique[a]

	Ca/P ratio								
	0.65	0.6	0.55	0.5	0.45	0.4	0.35	0.3	0.25
Coarse powder									
E_{a_1} (kJ mol^{-1})	314.7	337.3	329.0	297.6	262.0	331.4	307.1	356.9	359.3
E_{a_2} (kJ mol^{-1})	298.9	321.5	313.0	282.0	246.6	315.0	302.5	340.3	343.1
E_{av} (kJ mol^{-1})	306.8	329.4	321.0	289.8	254.3	323.2	336.3	348.6	351.2
mE_a (kJmol^{-1})	750.7	672.7	802.2	911.4	258.3	212.4	225.0	153.3	200.7
m	2.447	2.042	2.499	3.145	1.016	0.657	0.669	0.440	0.571
Fine powder									
E_{a_1} (kJ mol^{-1})	371.4	354.6	419.6	338.4	409.2	308.5	289.3	598.3	287.4
E_{a_2} (kJ mol^{-1})	356.2	339.5	404.6	323.6	394.5	293.5	275.1	591.1	272.5
E_{av} (kJ mol^{-1})	363.8	347.1	412.1	331.0	401.9	301.0	282.2	594.7	280.0
mE_a (kJ mol^{-1})	755.9	429.0	896.6	691.2	448.0	273.6	206.5	318.0	154.9
m	2.078	1.236	2.176	2.088	1.115	0.909	0.732	0.530	0.553

[a] E_{a_1}: $\ln(\beta/T_p^2)$ vs. $(1/T_p) \times 10^4$, E_{a_2}: $\ln(\beta)$ vs. $(1/T_p) \times 10^4$, $E_{av} = (E_{a_1} + E_{a_2})/2$; mE_a: $\ln(\Delta T)$ vs. $(1/T) \times 10^4$, $m = mE_a/E_{av}$.

isothermal crystallization glasses. β is the heating rate of DTA runs, E_c is the activation energy of crystal growth, T_p the exothermic peak temperature of DTA curves, and R the gas constant. The numbers n and m are dependent on the morphology of the devitrification, which in the Kissinger plot $n = m = 1$. If the value of the degree of crystallization at the peak temperature is not dependent on the heating rate, Eq. (1) becomes:

$$\ln(\beta) = -E_c/RT_p + \text{const.} \tag{2}$$

If the deflection from the baseline, ΔT, is proportional to the instantaneous reaction rate in the initial part of DTA crystallization peak, the change in the temperature has a much greater effect than the degree of crystallization on ΔT, Eq. (1) also gives

$$\ell n(\Delta T) = -mE_c/RT + \text{const.} \tag{3}$$

Table 2 lists the activation energies of crystal growth and the values of m for CaO/P_2O_5 glasses with Ca/P molar ratios from 0.25 to 0.65, the value of parameter m decreased sharply when the Ca/P molar was lower than 0.45; this indicates that the devitrification mechanism of these glasses trend to surface nucleation. And the activation energy of crystal growth of CaO/P_2O_5 glasses with various Ca/P molar ratios, are close to the isothermal crystallization data of $Ca(PO_3)_2$ glass powder (for particle size between 44 and 74 μm, presented by Abe et al. [7], $E_c = 120$ kcal mol^{-1} which was estimated by the relation between $t_{0.5}$ and temperature) and the results of this work agree with Costantiwi [8]. $E_c = 128 \pm$

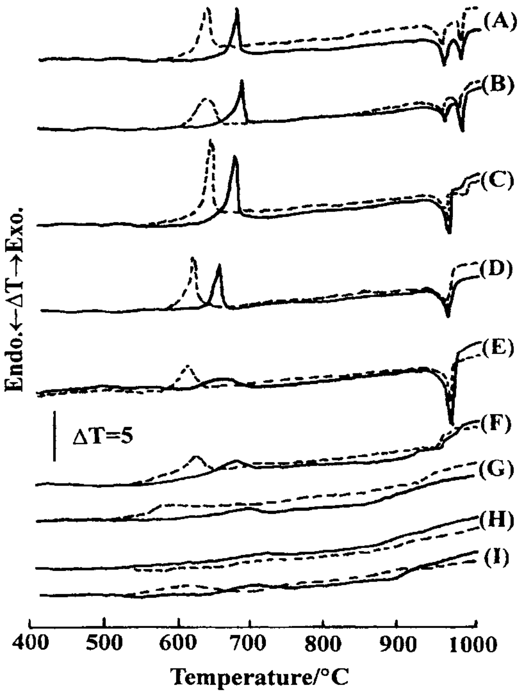

Fig. 1. The DTA curves of fine and coarse powder for calcium phosphate glasses with various Ca/P molar ratios: (A) Ca/P = 0.65, (B) Ca/P = 0.60, (C) Ca/P = 0.55, (D) Ca/P = 0.50, (E) Ca/P = 0.45, (F) Ca/P = 0.40, (G) Ca/P = 0.35, (H) Ca/P = 0.30, (I) Ca/P = 0.25, at static air atmosphere with a 10°C min^{-1} heating rate.

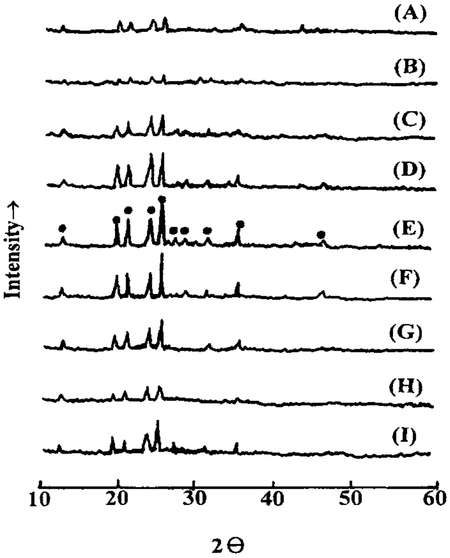

Fig. 2. The X-ray powder diffraction patterns of the crystalline form of calcium phosphate glasses with various Ca/P molar rations: (A) Ca/P = 0.65, (B) Ca/P = 0.60, (C) Ca/P = 0.55, (D) Ca/P = 0.50, (E) Ca/P = 0.45, (F) Ca/P = 0.40, (G) Ca/P = 0.35, (H) Ca/P = 0.30, (I) Ca/P = 0.25; (●) β-$(PO_3)_2$ whiskers.

14 kcal mol^{-1}, for the glass of composition CaO $0.1P_2O_5$ $0.9SiO_2$.

Fig. 1 shows the DTA curves of calcium phosphate glasses with Ca/P molar ratios from 0.25 to 0.65. The baseline shift at about 550°C is the glass transition temperature (T_g), for the calcium phosphate glass with Ca/P molar ratio larger than 0.45, but the T_g of calcium phosphate glasses become un-discernible and shift to lower temperature when the Ca/P molar ratio becomes smaller than 0.45. An exothermic peak occurs at about 600–700°C for all glasses, the exothermic peaks are sharp and the width of peaks are narrow for calcium phosphate glasses with molar ratio larger than 0.45. With the decrease in the Ca/P molar ratio of calcium phosphate glasses, the exothermic peaks become broad and the highness of peak is lower. And the melting peaks are also un-discernible and trend to lower temperature. In general, the exothermic peak of DTA curves for a coarse sample give more sharply than that for a fine sample at same experimental condition, that is in surface-nucleating glasses, the exothermic peak of crystallization position strongly dependent on the particle size used. Fine glass powders with higher surface area will crystallize at lower temperature so that the crystallization peak shifted to lower temperature. With efficient bulk-nucleation, the effect of particle size upon the position for the crystallization peak is small.

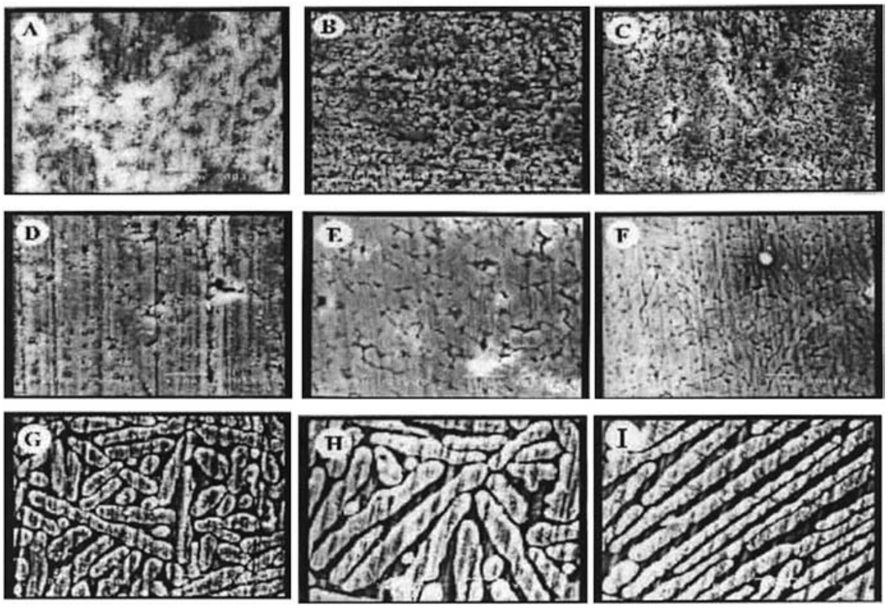

Fig. 3. Surface microstructure of crystallized calcium phosphate glasses with various Ca/P molar ratios: (A) Ca/P = 0.65, (B) Ca/P = 0.60, (C) Ca/P = 0.55, (D) Ca/P = 0.50, (E) Ca/P = 0.45, (F) Ca/P = 0.40, (G) Ca/P = 0.35, (H) Ca/P = 0.30, (I) Ca/P = 0.25.

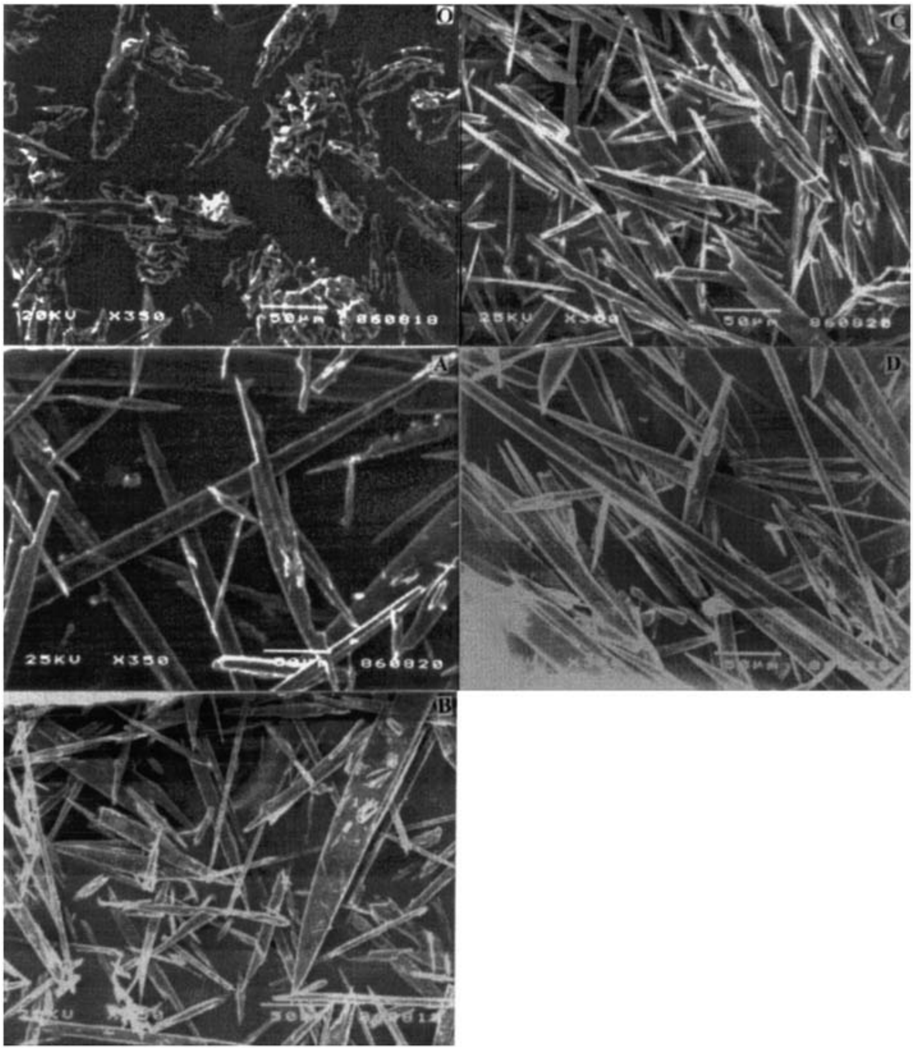

Fig. 4. The morphology of β-(PO$_3$)$_2$ whiskers: (O) crystallized glass powder >1180 μm; (A) crystallized glass powder after leaching process, 850–1180 μm; (B) crystallized glass powder after leaching process, 600–850 μm; (D) crystallized glass powder after leaching process, 75–600 μm; (E) crystallized glass powder after leaching process <75 μm.

To determine whether the devitrification begins at the surface or in the bulk of these glasses [9], we compared the peak temperatures of exothermic for coarse and fine particles. For the calcium phosphate glasses with Ca/P molar ratio smaller than 0.45, the exothermic peak temperatures occur at a considerably higher temperature for coarse particles than for fine, (see Fig. 1(F)–(I)): this result indicates surface nucleation mechanism was dominated in these glasses. And the parameters *m* listed in Table 2, which depend on mechanism and morphology are almost smaller than one or, more appropriately, nucleating at the surface of these glasses. But for the calcium phosphate glass with Ca/P molar ratio larger than 0.45, the exothermic peaks of coarse and fine particles were very close, (see Fig. 1(A)–(E)). At the same time, the parameters depend on mechanism and morphology are also larger than one. The results indicate bulk nucleation or, more appropriately, nucleation at the internal interface of these glasses. The XRD analysis of the resultant product of calcium phosphate glasses under sufficient nucleation and

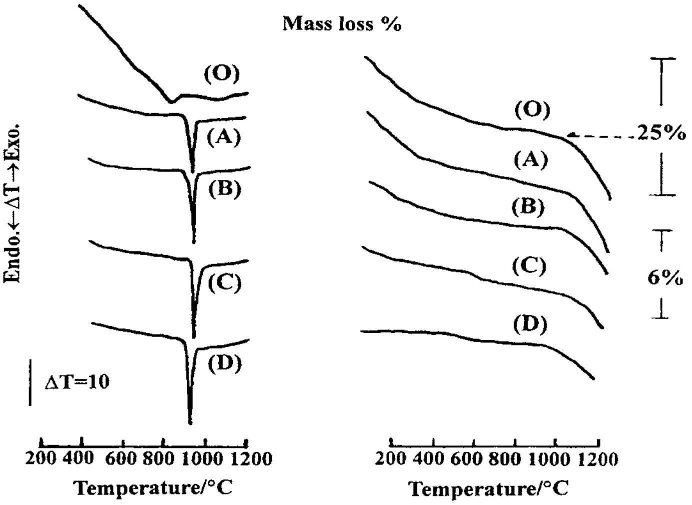

Fig. 5. DTA and TG curves of β-$(PO_3)_2$ whiskers.

crystallization process are shown in Fig. 2, the XRD patterns show that all of the diffraction peaks only to a crystalline-beta calcium metaphosphate (β-$Ca(PO_3)_2$), and the strongest intensities of diffraction peak appeared for the resultant product, which is the molar ratio equal: 0.45. But the intensities of diffraction peak were both decreased, when the Ca/P molar ratio was increasing or decreasing. The surface microstructure of the resulting products are shown in Fig. 3, β-$Ca(PO_3)_2$ crystalline was found to have a rod-like shape with 5–8 μm in diameter and 660 μm in length, the aspect ratios being 80–130. This result was also reported by Abe [2] in CaO/P_2O_5 glasses system with lower Ca/P molar ratio. It is more easy to obtain high aspect ratio β-$Ca(PO_3)_2$ crystalline in lower Ca/P molar ratio calcium phosphate glasses. β-$Ca(PO_3)_2$ crystalline were successfully extracted from crystallized calcium phosphate glasses by leaching with distilled water, the crystals of aspect ratios (16–400) were obtained from the crystallized glasses of which molar ratio of Ca/P is less than 0.4. Fig. 4 shows the morphology of crystallized calcium phosphate glass powder after sieving and leaching with molar ratio of Ca/P = 0.25. The β-$Ca(PO_3)_2$ crystalline is not obviously on the morphology of Fig. 4(O), because of the existence of glass phase. But crystalline β-$Ca(PO_3)_2$ are easy to found from a morphology of crystallized calcium phosphate glass, which after leaching process (Fig. 4(A) and (B)). This result indicates that the extraction step is needed for preparation of high purity β-$Ca(PO_3)_2$ crystalline. Fig. 5 shows the DTA and TG curves of resultant glass powder for before and after leaching process. The curves of TG and DTA indicate that the resultant powder before extraction step gave a high mass loss percentage (approximation 14%) and melting completely at 900°C (with a broad endothermic peak in DTA curve). But the resultant powder obtained after extraction step gave only 1% mass loss in TG curve and melting completely at 980°C (with a sharp endothermic peak). This result also indicates, that the leaching process is good enough for the extraction of the β-$Ca(PO_3)_2$ crystalline and the melting temperature agrees with Kasug's result. [10] (β-$Ca(PO_3)_2$ fibrous crystal melt completely at 970°C). Glasses are excellent candidates as the matrix phases, because their fluidity at a desired temperature varies with composition. Dense β-$Ca(PO_3)_2$ reinforced calcium phosphate glass-matrix composites are believed to have potential as high-strength ceramics with low modulus of elasticity then the densification behavior of the fibrous products during hot pressing was monitored. The resultant glassy phase acted as a bonding agent to inter-link the fibers. β-$Ca(PO_3)_2$ crystals began to melt during hot pressing at a temperature lower than the melting point. Therefore, the optimum heating temperature was determined by the thermal properties between matrix glass and β-$Ca(PO_3)_2$ fiber.

4. Conclusions

The crystallization mechanism of calcium phosphate glasses with molar ratio Ca/P = 0.25–0.65 were investigated in this work, the crystallization mechanism of calcium phosphate glass was changed from bulk nucleation to surface nucleation by decreasing the Ca/P molar ratio.

β-$Ca(PO_3)_2$ whiskers were successfully extracted from crystallized calcium phosphate glass powder by leaching with distilled water, the whiskers of aspect ratios (16–400) were obtained from the crystallized glass powder of which molar ratio of Ca/P = 0.25 after leaching process. Then leaching process is good for purification of β-$Ca(PO_3)_2$ crystalline, and the thermal properties of β-$Ca(PO_3)_2$ whiskers are important in preparation of a fiber-reinforced glass-ceramics composite.

References

[1] Y. Abe, Phosphorus Research Bulletin 1 (1991) 317–332.

[2] T. Kasuga, A. Ichino, Y. Abe, J. Ceram. Soci. Jpn. 100(8) (1992) 1088–1089.

[3] E.J. Griffith, Proc. 1981 Intern'l. Conf. Phos. Chem. 1981, pp. 361–365.

[4] C.P.A.T. Klein, Y. Abe, Hosono, K. DE Groot, Biomaterials 5 (1984) 362–364.

[5] C.P.A.T. Klein, Y. Abe, Hosono, K. DE Groot, Biomaterials 8 (1987) 234–236.

[6] T. Ozawa, J. Therm. Anal. 7 (1975) 601.

[7] Y. Abe, T. Arahori, A. Naruse, J. Am. Ceram. Soc. 59(11/12) (1976) 487.

[8] A. Costantiwi, R. Fresa, A. Bari, F. Bramda, Thermochim. Acta 280/281 (1996) 237.

[9] A.H. Kumar, R.R. Tummla, Am. Ceram. Soc. Bull. 57 (1978) 738.

[10] T. Kasuga, Y. Ota, K. Jsuji, Y. Abe, J. Am. Ceram. Soc. 79(7) (1996) 1821–1824.