Developmental Study of Functional Glass Ceramics

Part 3 A Synthesis of Binary CaO/P_2O_5 Glass Ceramics

Yuuji Nomura, Kunio Wakasa, Yasuhiro Yoshida, Atsuharu Ikeda, Yasuhiko Yamasaki, Moin Jan Chowdhury*, Nurhayaty Natsir*, Ken-ichi Shirai*, Masayuki Yoshioka*, and Masao Yamaki

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ABSTRACT

A synthesis of new ceramics was tried using binary CaO/P_2O_5 glass ceramics which were mixed or melted to glass state, to compare with an apatite-based glass ceramic, 20 wt% CaO/10 wt% P_2O_5/10 wt% MgO/10 wt% Al_2O_3/50 wt% SiO_2 as a reference material. First, binary CaO/P_2O_5 powders were mixed as powder mixtures, and secondly they were synthesized with 5, 10, 15, 20, 25, 30 and 35 wt% of CaO, based on thermal analysis results, whereas both pure minerals of CaO and P_2O_5 were used. Thermal endothermic and exothermic reactions of their powder mixtures and glass ceramics were examined by differential thermal analysis (DTA) and thermogravimetry (TG) during a heat to 1200 or 1100°C. Because of heating rate-dependent reactions of cryatal formation in apatite-based glass ceramics, thermal (ceramming) treatment of binary CaO/P_2O_5 was determined to be 1000°C. This study showed that the crystallization temperature ranges of the amorphous glass matrix were detected by thermal analyses and the appropriate ranges of CaO content in binary new ceramics were clarified for dental application.

Hiroshima University School of Dentistry, Department of Dental Materials (Chairman; Professor Masao Yamaki).

* Hiroshima University School of Dentistry, Department of Operative Dentistry (Chairman; Professor Hideaki Shintani).

Correspondence to; Dr *K. Wakasa*, Hiroshima University School of Dentistry, Department of Dental Materials, Kasumi 1-chome, Minamiku, Hiroshima City, 734 Japan.

INTRODUCTION

Developmental study of functional glass ceramics has been done using apatite-based glass ceramic[1] and powder ceramics[2]. Dental feldspathic and aluminous porcelains were used as the esthetic purpose[3], and all-ceramic restorative crowns showed mechanical strengths and toughness than dental conventional porcelains[4], because of less strength of porcelain-fused-to metal crowns[5,6]. The earlier reports described that newly-designed apatite-based glass ceramics had the mechanical properties of apatite-based glass ceramic had enough magnitudes to toughen the amorphous glass matrix by the ceramming treatments[7-12]. The effect of thermal treatment for nucleation on the crystallization of glass ceramics was examined to strengthen the amorphous glass matrix[13-17]. It is known that TiO_2 or CaF_2 is effective to crystallize the matrix of $SiO_2/MgO/Al_2O_3$ glasses and the crystallization occurrs in the glass transition temperature ranges[13]. In the glass ceramic systems[14-17], the microcracking stability was obtained when the formation of a microcrack zone occurred at the tip of a propagating crack. That is, the microstructure within the amorphous glass matrix had the role of the stable crack propagation. Earlier reports said that calcium metaphosphate or calcium phosphate glass was prepared as $CaO/P_2O_5/H_2O$ or CaO/P_2O_5 mixture having such a microstructure by melting them[18-20]. From these recent works, the synthesis of binary CaO/P_2O_5 glass ceramics was carried out as this developmental study of newly-designed glass ceramics.

MATERIALS AND METHODS

1. A synthesis of glass ceramics

The glass ceramic used as a reference material in this study was a newly - designed apatite - based 20 wt% CaO/10 wt% P_2O_5/10 wt% MgO/10 wt% Al_2O_3/50 wt% SiO_2 glass ceramic[5-10], which was melted within a platinum-crusible by high-frequency melting method[6]. The binary glass ceramics of CaO/P_2O_5 were synthesized with the CaO/P_2O_5 ratios of 0/100, 1/19, 1/9, 3/17, 1/4, 1/3, 3/7, 7/13, and 100/0. The CaO percentages were 0, 5, 10, 15, 20, 25, 30, 35, and 100 wt%. The synthesis condition was referred, based on the CaO/P_2O_5 phase diagram[13].

Their samples were powder mixtures and thermally-treated (cerammed) ones. The former were heated to 1200° C at heating rates of 5 and 20° C/min, whereas the latter heated to 1100° C at a heating rate, 20° C/min. The former and the latter ones were, respectively, cerammed at 980° C for 2hr and 1000° C for 2 and 6 hr.

2. Thermal analysis and X-ray diffraction analysis

DTA and TG analyses of the powder mixtures and cerammed samples were carried out using DT 30 and also DT 50 (Shimadzu Co, Kyoto, Japan). The measuring conditions were used, according to the early reports[1,2]. On the differential thermal analysis (DTA) curves, endothermic and exothermic reactions were examined. The endothermic peak temperatures were related to thermal decomposition and melting[1,2,9] and the exothermic peak temperature was related to crystallization process[2,12]. Also, the glass transition temperature, Tg, which occurred the change of slope of DTA curves, was measured. On thermogravimetry (TG) curves, the temperature ,T_{WL}, which initiated the weight loss of the samples, was measured, and the weight loss (TG %) was obtained. X-ray diffraction analysis of the cerammed binary CaO/P_2O_5 samples (1000° C for 2hr) was carried out in the 2θ range of 12 to 38 degree by XD-D1 (Shimadzu Co) at the same condition as the earlier report[12].

RESULTS

Figure 1 shows DTA curves of apatite-based glass ceramic powders when heated to 1200° C at heating rates of 5 and 20° C/min, and also Figure 2 shows DTA and TG curves of the glass ceramic powders which are treated at 980° C for 2 hr, when heated to 1200° C at a heating rate of 20° C/min. Their powders had an exothermic reaction (crystallization) in the temperture range of 850 to 1000° C and an endothermic reaction (melting) around 1100° C, as indicated by arrows. The heating rates affected their thermal behaviours, and the heating rate used in the following studies was 20° C/min. Figures 3 and 4, respectively, show TG and DTA curves of binary CaO/P_2O_5 glass ceramics (0 to 100 wt% CaO) when heated to 1100° C at a heating rate of 20° C/min. The decrease of weight loss was found for more CaO percent. After weight losses of the sample powders, the exothermic reaction occurred, although pure CaO had an endothermic recation around 650° C and also pure P_2O_5 powder had an endothermic recation around 400° C.

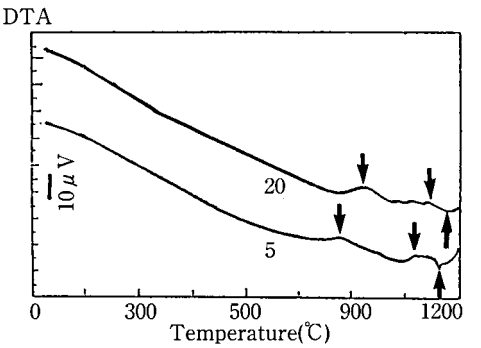

Figure 1 DTA curves of apatite-based glass ceramics when heated to 1200° C at heating rates of 5 and 20° C/min. The thermal reactions were indicated by arrows.

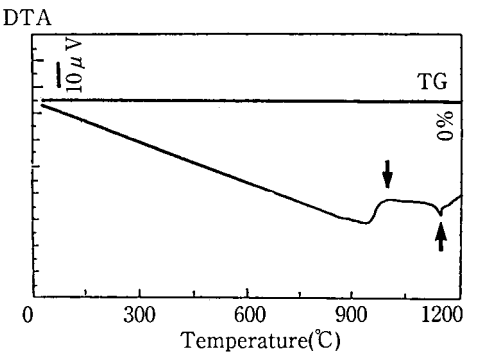

Figure 2 DTA and TG curves of apatite-based glass ceramic (980° C cramming treatment) when heated to 1200° C at a heating rate of 20° C/min.

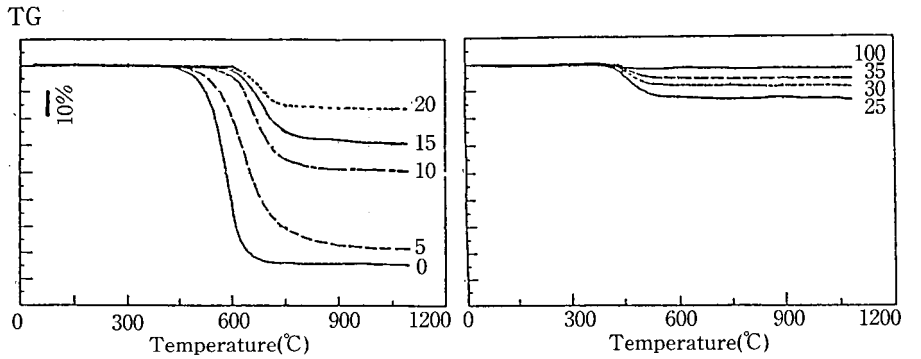

Figure 3 TG curves of CaO/P_2O_5 glass ceramics when heated to 1100° C at a heating rate of 20° C/min. The numbers mean CaO wt% in the powder mixtures.

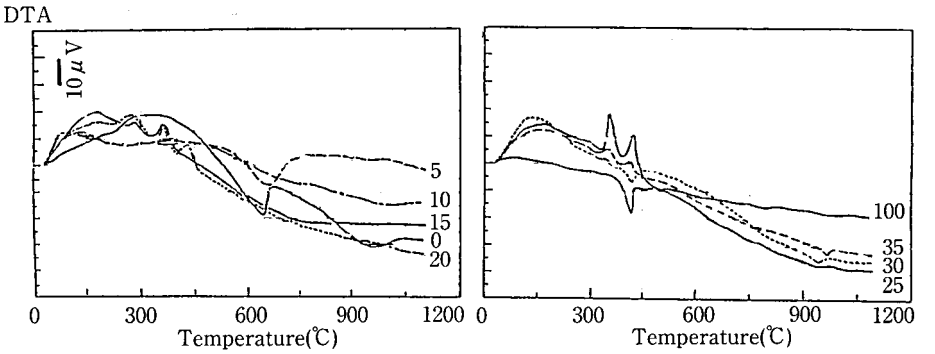

Figure 4 DTA curves of CaO/P_2O_5 glass ceramics when heated to 1100° C at a heating rate of 20° C/min. The numbers mean CaO wt% in the powder mixtures.

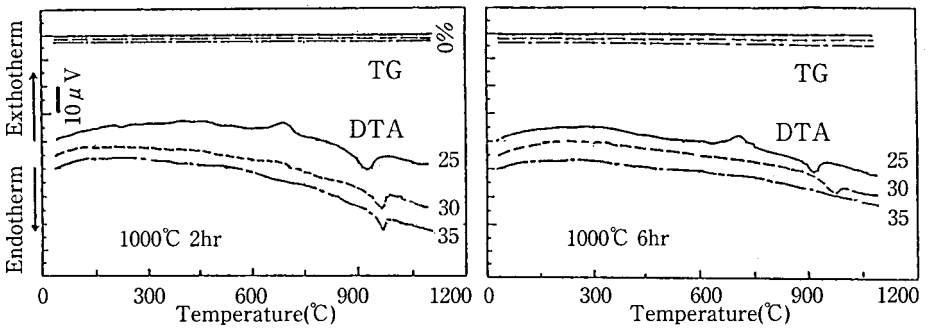

Figure 5 DTA and TG curves of CaO/P_2O_5 glass ceramics, which were thermally treated at 1000° C for 2 and 6 hr, when heated to 1100° C at a heating rate of 20° C/min. The numbers mean CaO wt% in the powder mixtures.

Figures 5 show DTA and TG curves of CaO/P_2O_5 glass ceramics with different CaO wt% (25, 30, and 35 wt% CaO) in the powder mixtures, which were thermally treated at 1000° C for 2 and 6 hr. Their samples were heated to 1100° C at a heating rate of 20° C/min. Using thermallly-treated powders, their thermal reactions were obtained clearly in the crystallization and melting temperature ranges. In Figures 6, the crystals were detected by X-

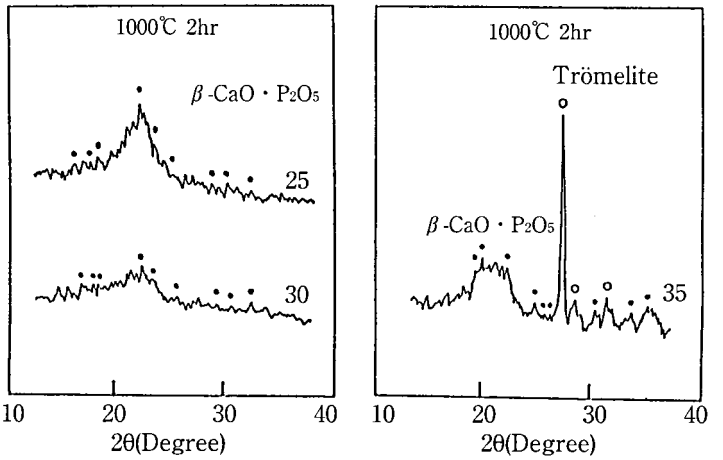

Figure 6 X-ray diffraction patterns of CaO/P_2O_5 glass ceramics which included 25, 30 and 35 wt% as a CaO content. The samples were treated at 1000° C for 2 hr.

ray diffraction analysis of CaO/P_2O_5 glass ceramics which included 25, 30 and 35 wt% as a CaO content. The samples used were the ones treated at 1000° C for 2 hr. The β-$CaO \cdot P_2O_5$ crystal was found for the samples including 25 and 30 wt% as a CaO content, and trömelite formed in the sample including 35 wt% as a CaO content associated with β-$CaO \cdot P_2O_5$ crystal.

The thermal analysis results are indicated in Tables 1 and 2. Glass transition temperature,Tg, on DTA curves was detected in binary CaO/P_2O_5 powder mixtures (Table 1). The Tg temperature increased when CaO was included in CaO/P_2O_5 mixtures. Table 2 indicates the characteristic temperature,T_{WL}, and TG in binary CaO/P_2O_5 powder mixtures, which were obtained on TG curves. T_{WL} which means the temerature where the weight loss initiates have the peak value at CaO = 15 wt%. The weight loss decreased from 74.8 to 7.0 wt% with more CaO prercent. Pure CaO had 1.9 wt% weight loss. Figure 7 is the melting temperatures of CaO/P_2O_5 glass ceramics with 0 to 100 wt% as a CaO content, showing that they changed from 650° C to around 1000° C with increasing CaO wt%. Pure CaO showed the highest value (2572° C) of the powder mixtures tested.

Table 1 Glass transition temperature, Tg, which was detected on DTA curves, in binary CaO/P_2O_5 powder mixtures. CaO/P_2O_5 ratio means the weight percent of binary powder mixtures.

CaO/P_2O_5	CaO (wt%)	Tg (°C)
0/100	0	473.3 (5.0)
1/19	5	510.7 (12.7)
1/9	10	562.7 (23.0)
3/17	15	541.0 (11.0)
1/4	20	533.3 (3.0)
1/3	25	534.0 (3.0)
3/7	30	542.5 (0.5)
7/13	35	541.7 (2.9)
100/0	100	377.7 (2.1)

Table 2 The characteristic temperature, T_{WL}, and TG in binary CaO/P_2O_5 powder mixtures, which were obtained on TG curves. CaO/P_2O_5 means the ratio of weight percent in binary powder mixtures. T_{WL} means the temperature where the weight loss initiates.

CaO/P_2O_5	CaO (wt%)	T_{WL} (°C)	TG (%)
0/100	0	511.3 (3.4)	74.8 (4.0)
1/19	5	556.0 (4.3)	64.4 (5.1)
1/9	10	621.7 (0.5)	39.3 (7.0)
3/17	15	630.0 (16.3)	28.5 (3.0)
1/4	20	428.7 (2.5)	14.7 (1.0)
1/3	25	423.3 (4.5)	12.4 (1.4)
3/7	30	404.5 (0.5)	7.6 (0.4)
7/13	35	413.3 (3.5)	7.0 (1.0)
100/0	100	406.7 (1.0)	1.9 (0.1)

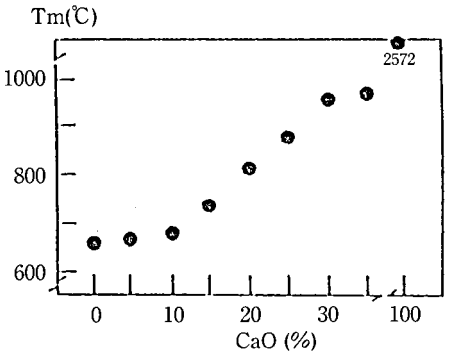

Figure 7 Melting temperatures of CaO/P_2O_5 glass ceramics with 0 to 100 wt% as a CaO content.

DISCUSSION

The thermal change of castable glass ceramic within the investment mould with decreasing test temperature from melting range affected the dimensional accuracy of cast ceramic crown or inlay, and the lower melting temperature gave the lower thermal change of cast glass restorations[1-3]. To apply such castable glass ceramics to dental restorations, dental investments used were ethyl silicate-bonded ones, as reported early[7,8]. In this study, as referred to CaO/P_2O_5 phase diagram[13], new calcium phosphate mixtures can be developed if the CaO content is selected. The glass formation and crystallization were examined by fundamental kinetics and X-ray diffraction[14-17]. The results clarified that the crystallization in the ceramic zone systems occurred through the nucleation and growth of rods and the crystallization rate depended on the thermal treatment temperature. These results suggest that the activation energy for nucleation is a function of composition and treatment temperature.

The glass formation range and cryatallization rate of calcium phosphate glass ceramics were examined the ceramming[18-21]. The results said that glass formation in CaO/P_2O_5 system was limited within the composition range less than 55/45 in molar ratio of CaO/P_2O_5. The thermal treatment condition obtained was 700°C for 5 hr. It is not a resonable condition for ceramming of dental glass ceramics because of longer holding time. Thus, CaO content range and ceramming temperature were examined using various weight ratios of CaO/P_2O_5, as indicated by 0/100 to 100/0 as a weight percent. In the earlier reports[18,19], 55/45 molar ratio corresponded to 27 wt% CaO in the binary glass ceramics. The treament condition selected in this study was 1000°C for 2hr, as compared with that at longer holding time (6 hr), because the same crystals formed at two conditions (Figs 4, 5, 6). The crystallization from the glass state took place at the glass transition temperature[22]. The CaO/P_2O_5 glass ceramics had the glass transition temperature range of 510.7 to 562.7°C (Table 1), and the exotherm of the crystallization was expected. As compared with CaO/P_2O_5 samples with 25, 30, and 35 wt% CaO as the powder mixtures (Fig 4) and cerammed glass (Fig 5), the crystallization ranges were found clearly on DTA curves in Fig 5 by the thermal treatment at 1000°C. This result agreed with apatite-based glass ceramics which had glass state (Figs 1, 2). This thermal analysis suggests that the maximum rate of crystal nucleation is needed for more growth of crystals. To obtain clearly the crystallization and precipitation of CaO/P_2O_5 glass ceramics, the oxide additives to them are important for additional dental applications.

SUMMARY

Dental binary glass ceramics, CaO/P_2O_5, whose crystals were formed within the glass matrix, were produced using powder mixtures and cerammed glass ceramics. These crystals were detected by thermal analysis during a heat to 1100°C. Most interesting results were that the effect of CaO in binary CaO/P_2O_5 powder mixtures and cerammed powders on thermal changes with test temperature was clarified. This study showed that the decomposition and crystal formation were respectively detected clearly as an endothermic peak and exothermic peak by DTA analysis. The CaO ranges (25 to 35 wt%) whose crystallization occurred were obtained clearly.

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