

# Thermal treatment and crystalline structure in dental cast ceramic materials

K. WAKASA\*

*University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, 1304 West Green Street, IL 61801, USA*

M. YAMAKI

*Hiroshima University School of Dentistry, Department of Dental Materials, 1-2-3 Kasumi, Minami-ku, Hiroshima, 734 Japan*

A. MATSUI

*Aoi Dental Center, 268-1, Nakashiroyama, Oike-kudaru, Fuya-machi, Nakagyo-ku, Kyoto, 604 Japan*

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The thermal treatment, known as 'ceramming', of cast glass ceramics was undertaken to clarify the crystalline microstructures that were observed at several constant temperatures. Differential thermal analysis when raising the test temperature indicated that the samples kept at 800, 890 and 980 °C had different characteristic temperatures. X-ray diffraction analysis and the Fourier transform-infrared method showed the findings of diopside,  $\beta$ -tricalcium phosphate and hydroxyapatite. These results suggest that the thermal ceramming temperature has to be selected for the conversion of amorphous glass ceramic materials in dental applications.

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## 1. Introduction

The formation of a crystal structure in amorphous glass ceramics has been attempted [1–7], and the characteristics of the crystal have been reported for glass ceramics of various chemical compositions, such as mica-based glass ceramics [1, 2, 7] and calcium phosphate glass ceramics, including a single hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  [4], and crystal compounds of mica and lithium alumina silica crystals [3, 5]. Because of the formation of crystals, as-cast material was thermally treated as follows: (1) after being heated at 400 or 500 °C for several hours, the specimens were held at 750 or 910 °C for several more hours [1, 2, 7]; (2) after heating at 750 °C for 30 min, the specimens were held at 870 °C for 1 h [4]; and (3) after heating at 750 °C for 2 h, the specimens were heated to 900 °C and held for several hours [3, 5]. These studies have barely clarified which kinds of crystal structures appeared during the thermal treatment; nor have they indicated at which temperature specific crystals were formed. Therefore, we need to determine which crystal structures are formed at high temperature by the transformation of the amorphous state (glass) to the ceramic state. The purpose of this study was to determine the conditions of the thermal treatment of experimental glass ceramics for dental purposes, and to determine the crystal structures formed at the treatment temperatures.

## 2. Materials and methods

The dental glass ceramic investigated was the experi-

mental  $\text{CaO-P}_2\text{O}_5\text{-MgO-SiO}_2$  system which was patented by one of the present authors (A. M.) and the Nippon Electric Glass Co. (Shiga). The size of the ceramic ingot (6.5 g) was approximately 13 mm in diameter and 21 mm in height. The chemical compositions were analysed by mass and found to be: 20% CaO, 10%  $\text{P}_2\text{O}_5$ , 10% MgO, 50%  $\text{SiO}_2$ , and each additive compound of  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{CaF}_2$ . The ceramic sample was cast into the specific investment mould ( $\alpha$ -quartz and  $\alpha$ -cristobalite mixtures as an investment powder and ethylsilicate solution as a bonding agent [8]) by an experimental air-pressure casting machine for ceramic casting (J. Morita Co., Kyoto).

The thermal treatment of dental ceramic was done at 800, 845, 890, 935 and 980 °C for 2 h, and thermal properties due to differential thermal analysis (DTA; DT-30, Shimadzu Co., Kyoto) when heated to 1200 °C from 22 °C were determined to clarify the temperature conditions of the thermal treatment (PROTOTYPE I Ceramming Furnace, J. Morita Co., Kyoto). The heating rate in the furnace was approximately 5 °C  $\text{min}^{-1}$ . As crystal structures were formed in the treated specimens, X-ray diffraction analysis (Rigaku thermoflex, Rigaku Co., Tokyo) and Fourier transformation and infrared method (FT-IR; RAD-RC, Rigaku Co., Tokyo) were carried out for ingot, as-cast and treated specimens. In particular, pure hydroxyapatite powder (WAKO CHEM, Osaka) was used to identify hydroxyapatite in thermally treated powder samples at each thermal temperature.

\* On leave from Hiroshima University.

### 3. Results

The DTA curves are shown in Fig. 1 ( $T_g$ , glass transformation temperature;  $T_c$ , crystallization temperature;  $T_m$ , melting temperature) and their results are given in Table I (average temperature).  $T_g$  ranged from 707 to 770 °C, and  $T_c$  was about 870–1000 °C as an exothermic peak. The materials melted near 1160 °C when heated at a rate of 5 °C min<sup>-1</sup>, showing an endothermic peak on the DTA curve.

The identification of the crystals that were formed by thermal treatment was done by means of X-ray

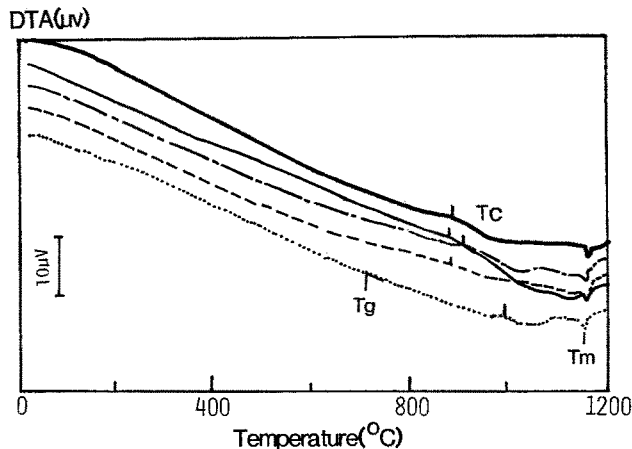


Figure 1 Differential thermal analysis curves of thermally treated materials, showing  $T_g$ ,  $T_c$  and  $T_m$ : (—) ingot, (—) as-cast, (—) 800, (—) 890, (—) 980 °C for 2 h.

TABLE I Thermal characteristic temperatures  $T_g$ ,  $T_c$  and  $T_m$  in materials treated thermally (see text for key)

Materials	Temperature (°C)		
	$T_g$	$T_c$	$T_m$
Ingot	737	879	1156
As-cast	770	873	1153
800 °C × 2 h	707	880	1158
890 °C × 2 h	727	911	1162
980 °C × 2 h	719	998	1158

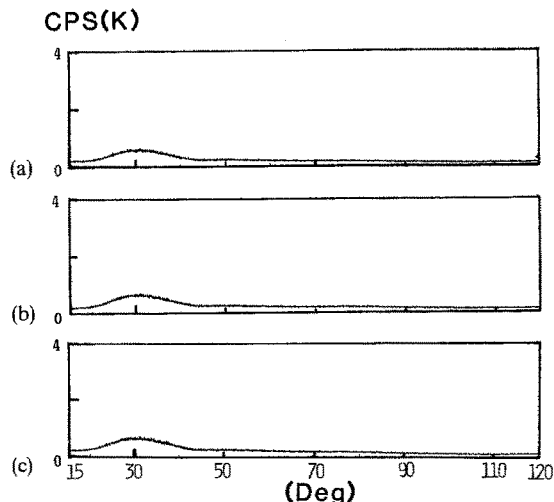


Figure 2 X-ray diffraction patterns of the samples tested. (a) As-cast, (b) 800 °C and (c) 845 °C for 2 h.

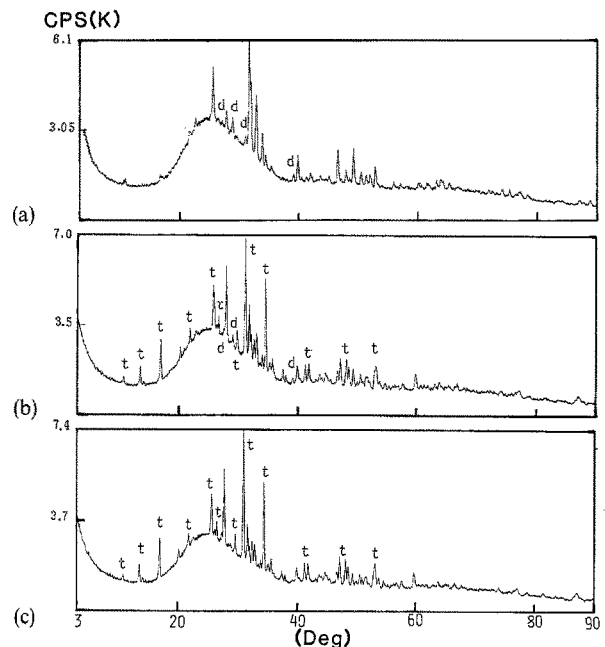


Figure 3 X-ray diffraction patterns of the materials treated thermally at (a) 890, (b) 935 and (c) 980 °C for 2 h. The HAp peak occurred at 890 °C, except for the portion of the d peak, and the HAp peak agreed with the t peak in some parts of (b) and (c). For key, see text.)

### Transmittance (%)

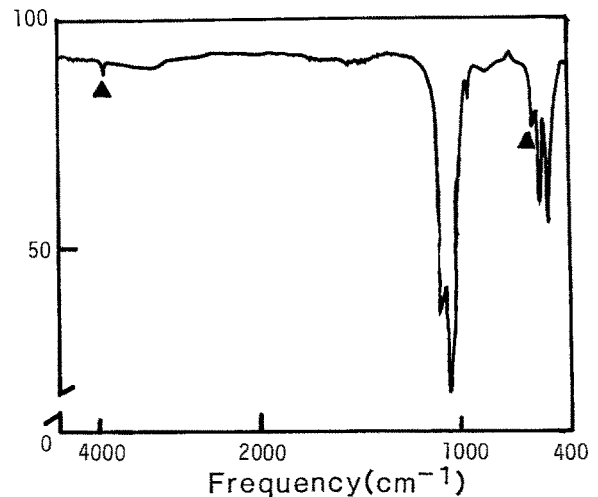


Figure 4 FT-IR peak of hydroxyapatite (▲ shows the evidence of appearance of hydroxyapatite on the FT-IR picture).

diffraction (Figs 2 and 3) and FT-IR method (Figs 4–6). The amorphous structure was detected for powders made from as-cast and thermally treated samples (800 and 845 °C). In samples treated at 890, 935 and 980 °C different patterns were observed (Fig. 3a–c). Hydroxyapatite (HAp) was mainly formed in the samples treated at 890, 935 and 980 °C for 2 h, but other crystals were observed. In Fig. 3a the treated sample (890 °C) had diopside (denoted by d) as  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ , and the sample (935 °C) was additionally composed of  $\beta$ -tricalcium phosphate (t;  $\beta\text{-}3\text{CaO} \cdot \text{P}_2\text{O}_5$ ). At 980 °C  $\beta$ -tricalcium phosphate also formed together with HAp, although diopside crystals were not observed. In the experimental glass ceramic tested, three types of crystals formed only at 935 °C. The finding of HAp powder was clarified as

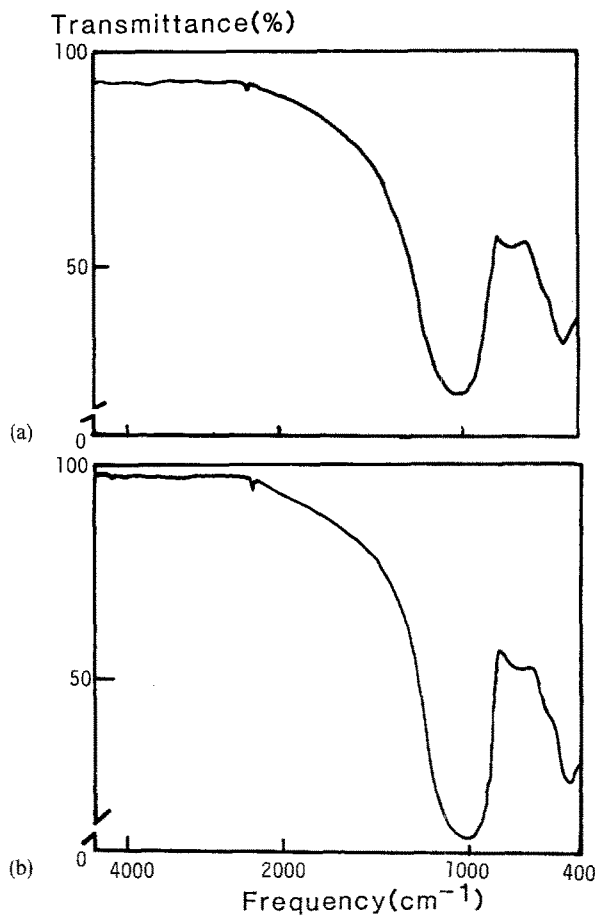


Figure 5 Examples of FT-IR peaks. (a) As-cast and (b) 800 °C thermal treatment.

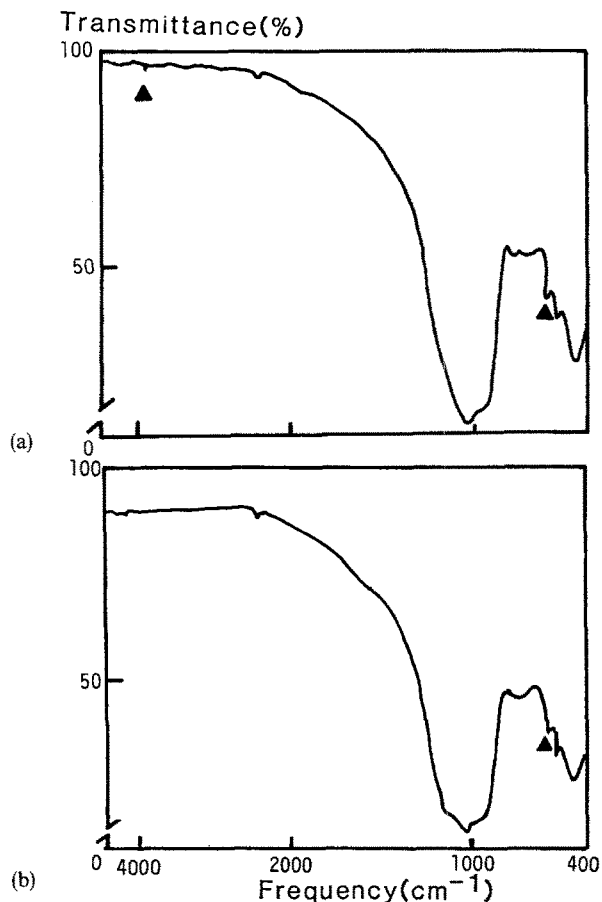


Figure 6 Examples of FT-IR peaks. (a) 890 and (b) 980 °C thermal treatment (for key, see text).

shown in Figs 4–6. On the basis of HAp in Fig. 4 the finding of HAp was observed for the treated samples at 890 and 980 °C. The FT-IR results agreed with the X-ray diffraction analysis.

#### 4. Discussion

Throughout the casting process the glass-ceramic material retains its amorphous structure [1–7]. The castings have to be converted to a partly crystalline state within amorphous glass by the ceramming thermal treatment. In the example of mica-type glass-ceramic, mica crystals nucleated and grew in the temperature-controlled conditions [7, 9]. The strength and fracture resistance increased because of the resultant microstructures [7–10]. Also, the crystals including fluoroapatite,  $(Ca_{10}(PO_4)_6(O, F_2))$  and  $\beta$ -wollastnite ( $\beta$ - $CaO \cdot SiO_2$ ) in the  $MgO-CaO-SiO_2-P_2O_5$  ceramic system, bonded to bone tightly because of the fluoride content [9]. These results mean that the present experimental glass-ceramic materials would be strengthened when the crystal formation occurred.

This study shows that the thermal heat treatment at each temperature gave different crystal structures to the experimental glass-ceramics tested (Figs 2–6). When almost the same heating rate as one in the furnace for ceramming was used in the thermally treated ceramic materials, the temperatures where crystalline formation was observed have to be selected, depending on its crystal. As-cast and ingot samples had nearly the same temperature ( $T_c$ ) as the sample heated at 800 °C. Because DTA results showed the occurrence of crystalline structures with increasing test temperature (Fig. 1), the as-cast sample when heated at each temperature would indicate the crystal formation within its casting. In treating its casting thermally after taking it out from the investment mould, higher ceramming temperatures than the glass-transition temperature (707–770 °C) led to the formation or softening of the casting under the macroscopic observation of castings. The result suggests that the ceramming heat treatment of castings has to be carried out within the mould. With this method the dental ceramic could keep the shape of the castings constant without changing its shape within the investment mould.

In the present study the state of crystalline microstructures had an important effect on the strength and the appearance. The colour, especially of the cast ceramic material, changed macroscopically to white because of the formation of crystallines, but the transparent state was not observed macroscopically with rising test temperature. This could strongly indicate that the crystal microstructures formed by ceramming treatment depend on the temperature conditions during the heat treatment.

We now hold the view that the fine crystalline structures in glass-ceramic materials could be changed by thermal treatment. This means that there are appropriate thermal treatment conditions which offer better mechanical strength without brittle fracture. As a first study of the present glass-ceramic material the relation between thermal treatment and structures

was examined. In such a material it would be possible to establish better thermal treatment conditions necessary to mechanical strength. We are trying to do this in subsequent experiments, because the effect of microstructural features on the strength of ceramics is not revealed in the present glass ceramics.

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