Preparation of Apatite-Containing Calcium Phosphate Glass-Ceramics

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Abstract A new type of glass-ceramic for novel dental fillers, which require excellent chemical durability, was investigated. Three types of glass-ceramics were prepared using compositions of 40CaO-xCaF2-(5-x)Na2O-25TiO2-30P2O5 (in mol%, x=0, 2.5, 5). With increasing CaF2 amount, both glass transition temperature and crystallization temperature increased. The glass-ceramics were prepared by a conventional two-step heating method. In 40CaO-5Na2O-25TiO2-30P2O5 glass-ceramic, Nasicon-type RTi2(PO4)3 (R=Na, 1/2Ca) and β-tricalcium phosphate (β-TCP) crystals were precipitated in the glass-ceramic. By incorporation of fluorine to the glass, the formation of β-TCP was controlled and fluoroapatite was found to be formed preferentially. In 40CaO-5CaF2-25TiO2-30P2O5 glass-ceramic, dissolution by acid-treatment was strictly controlled. In the present work, a new type of apatite-containing phosphate glass-ceramic without silica, based on the above-mentioned glass composition, could be newly prepared.

INTRODUCTION

Calcium phosphate ceramics such as hydroxyapatite (HAp) have been investigated as substitute materials for tooth and bone so far. In our earlier work, 42CaO-25TiO2-30P2O5-3Na2O glass-ceramic containing Nasicon-type RTi2(PO4)3 (R=Li, Na, 1/2Ca) and β-Ca3(PO4)2 (TCP) crystals was developed2,3; β-TCP is easily dissolved by acid-treatment, resulting in the preparation of porous glass-ceramics with a skeleton of Nasicon-type crystal. We are investigating this glass-ceramics for application to dental fillers.

For dental use, excellent chemical durability is required to the materials. The durability of β-TCP and HAp are insufficient as above-mentioned. On the other hand, fluoroapatite (Ca10(PO4)6F2; FAp) has higher chemical durability in comparison with HAp4. We anticipated that, if the soluble β-TCP crystal in the glass-ceramic would be altered into FAp crystal, the glass-ceramic could show excellent properties in use as dental applications. Almost all of apatite-containing glass-ceramics have been reported to be derived from silicate glasses so far.
In the present work, a new type of glass-ceramic containing FAp was prepared by the heat treatment of the phosphate glasses without silica containing fluorine.

EXPERIMENTAL

In the present work, three types of glass-ceramics were prepared using compositions of 40CaO-xCaF2-(5-x)Na2O-25TiO2-30P2O5 (in mol%, x=0, 2.5, 5). The batch mixture was prepared using raw materials such as reagent-grade CaCO3, Na2CO3, CaF2, TiO2, and H3PO4 (85% liquid). The mixture was put into a Teflon beaker with a small amount of water and stirred well to make a slurry. After the slurry was dried, the resultant product was melted in a platinum crucible at 1300 °C for 0.5 h in air. The melt was poured onto a stainless-steel plate and quickly pressed by an iron plate. As a result, plate-like glass pieces with thickness of 0.2 - 1 mm were formed.

The glasses were heated at an elevating rate of 5 °C/min from room temperature to 660 – 700 °C and held at the temperature for 24 h for the nucleation, and subsequently they were elevated to 710 – 755 °C for 12 h for the crystal growth. The heat-treatment temperatures were determined from differential thermal analysis (DTA). Crystalline phases precipitated in the glass-ceramics were examined by powder x-ray diffractmetry (XRD) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Fig. 1 shows the DTA curves of 40CaO-xCaF2-(5-x)Na2O-25TiO2-30P2O5 glasses. With increasing CaF2 amount, both glass transition temperature (Tg) and crystallization temperature (Tc) increased. From the curves, the heat-treatment temperatures for the glasses were determined as shown in Table 1. The heat-treatment temperature for the nucleation (T1) is the halfway temperature between Tg and Tc, and that for the crystal growth (T2) is around Tc in the DTA curve.

Fig. 2 shows XRD patterns of 40CaO-xCaF2-(5-x)Na2O-25TiO2-30P2O5 glass-ceramics prepared by the two-step heat-treatment shown in Table 1. In the patterns of 40CaO-5Na2O-25TiO2-30P2O5 glass-ceramic, sharp peaks assigned to Nasicon-type crystal are seen. The peaks assigned to β-TCP and
**Table 1. Heating temperatures for 40CaO-xCaF2-(5–x)Na2O-25TiO2-30P2O5 glasses.**

<table>
<thead>
<tr>
<th>Mother glass composition [mol%]</th>
<th>T1 [°C]</th>
<th>T2 [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>660</td>
<td>710</td>
</tr>
<tr>
<td>x = 2.5</td>
<td>670</td>
<td>720</td>
</tr>
<tr>
<td>x = 5</td>
<td>700</td>
<td>755</td>
</tr>
</tbody>
</table>

The glasses were heated by the process with durations at T1 for 20h and at T2 for 12h. T1 and T2 are temperatures for the nucleation and crystal growth, respectively.

(TiO)2P2O7 crystals are also seen. On the other hand, in 40CaO-2.5CaF2-2.5Na2O-25TiO2-30P2O5 glass-ceramic, FAp and TiO2 (anatase) crystals were precipitated in addition to Nasicon-type crystal, β-TCP and (TiO)2P2O7 crystals. In the pattern of 40CaO-5CaF2-25TiO2-30P2O5 glass-ceramic without Na2O, the strong peaks assigned to fluoroapatite crystal are seen with those of low intensities of Nasicon-type and TiO2 (anatase) crystal. By addition of CaF2, FAp was found to be formed preferentially. On the other hand, the formation of β-TCP was controlled.

The glass-ceramics were treated with 1-N HCl aq. for 5 min at room temperature to observe their microstructures. Fig. 3 shows SEM photos after the HCl-leaching of 40CaO-xCaF2-(5–x)Na2O-25TiO2-30P2O5 glass-ceramics. In 40CaO-5Na2O-25TiO2-30P2O5 glass-ceramic, after the treatment, dendrite-like morphology is seen. Our earlier work showed that the leaching of the surface originates from dissolution of soluble calcium phosphates such as β-TCP in the glass-ceramic. In 40CaO-5CaF2-2.5Na2O-25TiO2-30P2O5 glass-ceramic, the closely packed, small-sized morphology is seen. The leaching is closely related to the formation of β-TCP in the glass-ceramic. On the other hand, in 40CaO-5CaF2-25TiO2-30P2O5 glass-ceramic, no dendrite-like surface is seen; almost no dissolution seems to occur. Incorporation of fluorine to the glass composition induces the formation of FAp and controls the β-TCP formation. In Fig. 3(c), small-sized pits are seen. The pits are believed to originate from dissolution of residual glassy phase in

![Fig. 2. XRD patterns of 40CaO-xCaF2-(5–x)Na2O-25TiO2-30P2O5 glass-ceramics prepared by a two-step heat-treatment.](image-url)

- ○:MTi4(PO4)6 (M: 1/2Ca, Na), □:TiO2,
- ◎:Ca5(PO4)3F, ☆:(TiO)2P2O7,
- ●:β-Ca3(PO4)2, ×:Unknown

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the glass-ceramic.

**SUMMARY**

In the present work 40CaO-5CaF$_2$-25TiO$_2$-30P$_2$O$_5$ glass-ceramic was found to have excellent chemical durability, which originates from FAp formation. Incorporation of fluorine to the glass controls the β-TCP formation in the glass-ceramic to induce the FAp formation. Further work is in progress to develop novel dental fillers using a new type of apatite-containing phosphate glass-ceramic without silica.

**REFERENCES**


Fig. 3 SEM photos after the HCl-leaching of 40CaO-xCaF$_2$-(5-x)Na$_2$O-25TiO$_2$-30P$_2$O$_5$ glass-ceramics.
(a) $x = 0$, (b) $x = 2.5$ and (c) $x = 5$