

Surface Modification of Bioactive Calcium Pyrophosphate Glass-Ceramics

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Silica-free calcium pyrophosphate glass-ceramics with easy machinability were recently developed by crystallization of the $60\text{CaO}-30\text{P}_2\text{O}_5-7\text{Na}_2\text{O}-3\text{TiO}_2$ glass; $\beta\text{-Ca}_3(\text{PO}_4)_2$ ($\beta\text{-TCP}$) and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ ($\beta\text{-CPP}$) crystalline phases are included in the glass-ceramic. Bonelike apatite formation was observed on the glass-ceramic after 20 days of soaking in simulated body fluid (SBF); the glass-ceramic was suggested to show bioactivity. The apatite-forming ability of the glass-ceramic can be easily improved by autoclaving in water. When the autoclaved sample was soaked in SBF, bonelike apatite began to form after 3 days. After 10 days of soaking, the surface of the sample was completely coated with the apatite. On the other hand, no apatite formed on the glass-ceramic, which was not autoclaved, even by soaking in SBF for 10 days. During the autoclaving, titanium ions in the amorphous phases around the surface form crystalline phase (anatase) and hydrated titania groups, which may play an important role in the apatite formation.

Key words: Glass-ceramic, Autoclave, Calcium phosphate, Apatite, Simulated body fluid

1. INTRODUCTION

Calcium phosphate ceramics such as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) or $\beta\text{-Ca}_3(\text{PO}_4)_2$ ($\beta\text{-TCP}$) show high biological compatibility and safety in living tissues. These ceramics, however, do not have sufficient performances in mechanical properties such as bending strength, fracture toughness or machinability. Some works on microstructural improvement by introducing fibers or particles into matrix phase have resulted in improved mechanical properties such as the strength or the toughness. Few works, however, has been done to study improvement of the machinability. If the ceramics could be machined using conventional tools, they would be used for various applications to surgical or dental fields.

Some mica-containing glass-ceramics have been known to show good machinability¹ that is the ability to be cut, sharpened, planed off or scrapped off using conventional tools. Machinable glass-ceramics for biomedical use have been reported to be prepared by precipitation of apatite and mica crystals in a glass during heat treatment.² The easy machinability of the ceramics results from the cleavage of interlocking mica crystals precipitated in the glass.³

However, almost no phosphate ceramics having machinability have been prepared so far. We noted that $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ ($\beta\text{-CPP}$) crystal belongs to a tetragonal, space group $P4_1$,⁴ and the ab plane is spread by a three-dimensional sheet consisting of $\text{P}_2\text{O}_7\text{-Ca}$ infinite chains based on the chelatelike rings, giving a matted effect when viewed down to the c axis.⁵ It was anticipated that the crystal structure of $\beta\text{-CPP}$ having matted sheets may induce a cleavability of the crystal; novel calcium phosphate bioceramics having machinability may be prepared by including $\beta\text{-CPP}$ crystal.

In general it is difficult to prepare dense $\beta\text{-CPP}$

ceramics using a conventional powdery sintering process. One of the most promising processes to obtain materials containing a large amount of $\beta\text{-CPP}$ crystal is believed to be a glass-ceramic method. Glass-based materials have advantages in that they can be allowed some latitude in choice of the compositions and that microstructure of the crystallized glasses can be improved under various heating conditions. It is necessary to obtain calcium phosphate glasses in the pyrophosphate region for preparation of $\beta\text{-CPP}$ glass-ceramics.

Recently, we found that SiO_2 -free calcium phosphate glasses in the pyrophosphate region can be obtained by introducing small amounts of Na_2O and TiO_2 ,⁶ and successfully new glass-ceramics containing $\beta\text{-TCP}$ and $\beta\text{-CPP}$ crystals.^{7,8} The glass-ceramic was found to be easy to machine using conventional tools.

The glass-ceramic forms bonelike apatite crystal on its surface after 20 days of soaking in simulated body fluid (SBF), which is a tris-buffer solution with inorganic ion concentrations of which are adjusted to be almost equal to those of human plasma, at 37°C ;⁹ the apatite formation may be closely related to bonding ability of the glass-ceramics to living bone. The apatite formation, however, did not occur within 10 days.⁹ Surface modification for enhancement of the apatite-forming ability may induce high bioactivity of the glass-ceramic. Body fluid or SBF are already highly supersaturated with respect to the apatite. The apatite formation on the glass-ceramic would be associated with presence of plentiful inducers for the apatite nucleation around the surface.¹⁰ Some groups such as Si-OH , Ti-OH , PO_4H_2 , or COOH are known as the promising candidates for supplying inducers for the apatite formation.¹¹ A hydrothermal process may be one of the promising methods for introducing the sufficient hydrated functional groups as inducers for apatite formation

around the surface of the glass-ceramic. In the present work the apatite-forming ability of the glass-ceramic was found to be drastically enhanced after a hydrothermal treatment in water.

2. EXPERIMENTAL PROCEDURE

The calcium phosphate glass was prepared using a composition of 60CaO-30P₂O₅-7Na₂O-3TiO₂ in mol%. The mixture of the starting materials, which were reagent-grade CaCO₃, H₃PO₄ (85% liquid), Na₂CO₃ and TiO₂, was placed with water in a Teflon beaker and stirred to make a slurry. The slurry was dried at ~200 °C. The resulting product was melted in a platinum crucible at 1300 °C for 0.5 h. The melt was poured onto a stainless-steel plate and quickly pressed by an iron plate, resulting in the formation of glass plates with thicknesses of 0.5~1.0 mm. The glass pieces were pulverized by using a zirconia ball mill under 10 μm in diameter, and the resulting powders were pressed isostatically at 100 MPa to obtain a disk-shaped compact of 38-mm diameter by ~7-mm thickness. The powder compact was heated in air at 5 °C/min to 850°C for 3 h. The microstructure of the glass-ceramic was observed with scanning electron microscope (SEM) incorporating x-ray microanalysis using energy dispersive spectrometry (EDS). Three-point bending strength was measured at a loading rate of 0.5 mm/min under a span length of 20 mm by using a rectangular-prism-shaped specimen of ~3 by ~4 by ~30 mm polished using a 0.5-μm diamond paste. Machinability of the glass-ceramic was examined by a drilling test using a conventional carbide tool of 1.5-mm diameter at a rotation speed of 1800 rpm under a load of 19.6 N.

The glass-ceramic plate of 10 by 10 by 1 mm was autoclaved in 50 mL of distilled water (DW; pH~6) at 140 °C for 1 h. The glass-ceramic plate was soaked in 100 mL of SBF (consisting of 2.5 mM of Ca²⁺, 142.0 mM of Na⁺, 1.5 mM of Mg²⁺, 5.0 mM of K⁺, 148.8 mM of Cl⁻, 4.2 mM of HCO₃⁻, HPO₄²⁻ and 0.5 mM of SO₄²⁻ that included 50 mM of (CH₂OH)₃CNH₂ and 45.0 mM of HCl) at pH 7.4 at 37 °C. After the soaking, the surface was examined by thin-film x-ray diffractometer (TF-XRD) at a glancing angle of 1 ° and observed by SEM. The surfaces before and after the autoclaving were discussed using laser Raman spectroscopy. The spectra were obtained using the 514.5 nm line of an Ar⁺ laser as the exciting beam.

3. RESULTS AND DISCUSSION

3.1 Preparation of Machinable Calcium Pyrophosphate Ceramics

The glass-ceramic with the high density (the relative density; ~95 %) was prepared under the present condition. The glass-ceramic showed bending strength (σ_f) of 100~120 MPa on average. Fracture toughness (K_{IC} ; estimated using an indentation microfracture method) was 1.7 MPa·m^{0.5} on average. Fig. 1 shows the polished face and the spectra obtained by x-ray microanalysis using EDS from the labeled portions. The photo makes it clear due to different atomic number contrast of the phases precipitated that there exist bright portions (A, B) and a dark portion (C). The bright portions are phases consisting of calcium phosphates with small amounts of sodium and titanium elements.

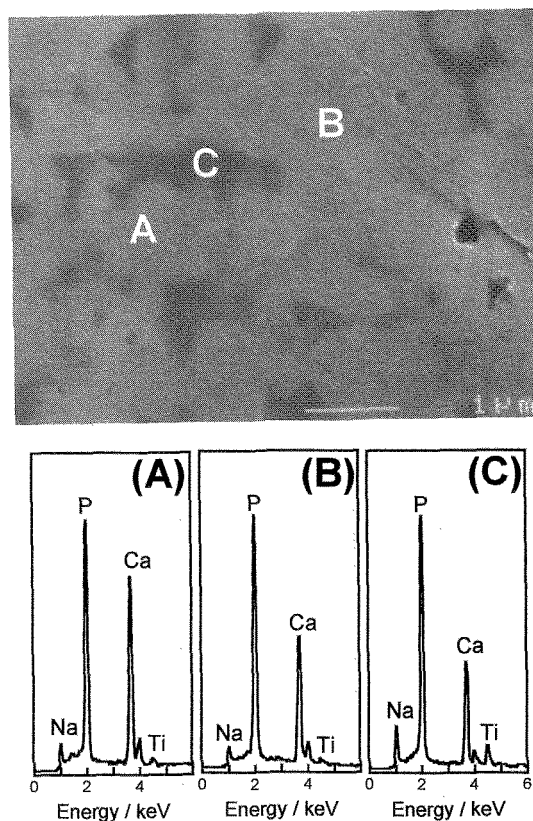


Fig. 1. SEM photo of the polished face of the glass-ceramic and EDS spectra from the labeled portions in the photo.

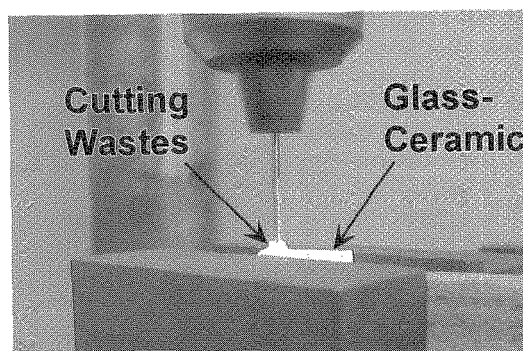


Fig. 2. Drilling test of the glass-ceramic. The glass-ceramic was gripped in a vise. Diameter of the tool is 1.5 mm.

The phase (A) is larger in the Ca content than that (B). β -TCP and β -CPP phases identified by XRD analysis are suggested to correspond to the phases (A) and (B), respectively. On the other hand, portion (C) contains larger amounts of elements such as sodium and titanium with a lower Ca content than portions (A) and (B). The phase (C) is believed to be formed by the partial melting which is related closely to the densification of the glass powders. Titanium element is mainly included in the glassy phase (C) and it is also done slightly in the calcium phosphate crystalline phases (A, B) as the amorphous phase, as described in 3.2.

The glass-ceramics in the present work could be drilled using a conventional carbide drill as shown in Fig. 2. Note that cutting wastes are observed on the specimen. The holes can be drilled successfully without chipping. The holes can be drilled successfully without chipping. The specimens were drilled at the rates of 0.3~0.5 mm/min. Although the value is not higher in comparison with that of a conventional mica-based machinable ceramic such as MACOR[®],¹ the glass-ceramic in the present work is the first calcium phosphate material that can be machined using a conventional tool, to our knowledge.

Fig. 3 shows an SEM photo of fracture face of the glass-ceramic. Plate-shaped products with several tens nanometers in thickness are piled up and they are interlocked with one another. The morphology is quietly similar to that of fracture face of mica-based machinable glass-ceramics. In machinable glass-ceramics consisting of cleavable mica crystals, cracks generated using an edged tool propagate through layered structure in mica crystals and subsequently branch off, resulting in formation of many small blocks due to the brittle microfracture. Easy machinability of the glass-ceramics in the present work is suggested to result from microstructure consisting of the interlocking plate-like β -CPP crystals dispersed in the glassy matrix phase. The machinability may imply a new finding that β -CPP crystal has cleavability.¹² The crystal structure of β -CPP having the matted sheets is suggested to be related closely to the cleavability.

When the glass-ceramics were prepared by prolonged heating (e.g., 8 h) or heating at higher temperatures (e.g., 950°C), serious chipping occurred around the holes drilled in the specimens.¹² The microstructures of specimens prepared by the prolonged heating or heating at higher temperatures developed exceedingly: grains and glassy matrix phase were grown into interconnecting three-dimensional networks. Some cracks may be propagated preferentially through the connective glassy phase with a low toughness and would cause the serious chipping in the materials during the drilling test. As the glassy phase does not develop largely in the glass-ceramic heated at 850°C for 3 h, it is suggested that cracks are apt to propagate through the interlocking β -CPP crystals; generation of the chipping in the glass-ceramic is restrained.

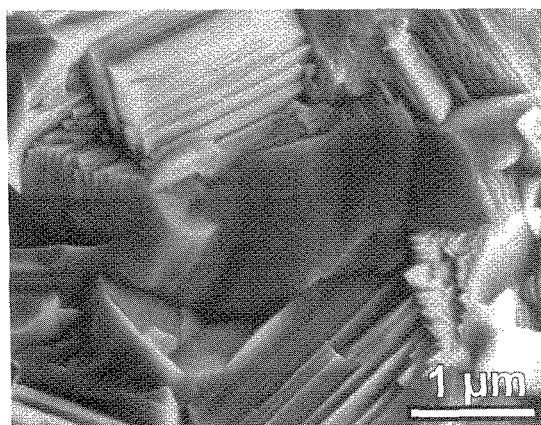


Fig. 3. Fracture face of the glass-ceramic.

3.2 Surface Modification of the Calcium Pyrophosphate Glass-Ceramic

A polished disk of the glass-ceramic was soaked in 50 mL of SBF for 20 days at 37°C. After the soaking, numerous deposition of leaf-like particles were observed.⁹ The new phase formed on the surface after the soaking are considered to be a bonelike apatite phase that is similar to the apatite in bone in its composition and structure, judged from the morphology and the TF-XRD and FT-IRRS spectra.^{7,8} This phenomenon may imply a possibility that the glass-ceramic shows bioactivity in living body. The apatite formation, however, did not occur within 10 days.⁹ Surface modification for enhancement of the apatite-forming ability may induce high bioactivity of the glass-ceramic. A hydrothermal process was found to be one of the promising methods for enhancement of the apatite-forming ability of the glass-ceramic.

Fig. 4 shows TF-XRD patterns of the glass-ceramic before and after the autoclaving in water and of the autoclaved sample after soaking in SBF for 10 days. No significant differences in the patterns between before and after the autoclaving are seen. The apatite formed on the the autoclaved glass-ceramic after 10 days of soaking in SBF. Fig. 5 shows SEM photos of the surface of the autoclaved glass-ceramic after 3~10 days of soaking in SBF, respectively. After 3 days of soaking, some small-sized depositions started to form newly on the sample. After 7 days, many depositions formed. After 10 days, the surface was completely covered with the

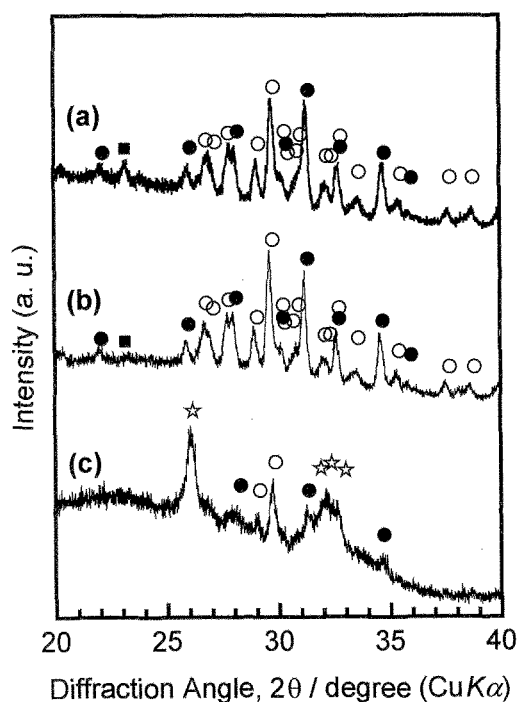


Fig. 4. TF-XRD patterns of the glass-ceramics before and after the autoclaving. (a) the as-prepared glass-ceramic, (b) the autoclaved glass-ceramic before soaking in SBF, and (c) the autoclaved glass-ceramic after (c) 10 days of soaking in SBF. (○); β - $\text{Ca}_2\text{P}_2\text{O}_7$, (●); β - $\text{Ca}_3(\text{PO}_4)_2$, (☆); apatite, and (■); unknown phase.

depositions. They are bonelike apatite, judged from both the TF-XRD pattern (Fig. 4(c)) and the morphology.¹³ Meanwhile, no apatite formed on the glass-ceramic, which was not autoclaved, after soaking in SBF for 10 days.⁹ The apatite-forming ability of the glass-ceramic was found to be enhanced after the autoclaving.

In our earlier report,¹⁴ x-ray photoelectron spectra (XPS) of the glass-ceramics before and after the autoclaving were measured. No significant changes in

the XPS spectra such as Ca_{2p} and P_{2p} are seen. The peak intensity of Na_{1s} spectrum decreased drastically after the autoclaving. This change shows that a large amount of Na^+ ion in the glassy phase around the surface of the glass-ceramic dissolves into water during the autoclaving. In the Ti_{2p} spectrum before the autoclaving, the peaks were seen at 459.6 eV and 465.5 eV, which correspond to those observed in an XPS spectrum of the mother glass.¹⁵ After the autoclaving, the Ti_{2p} peaks at 459.6 eV

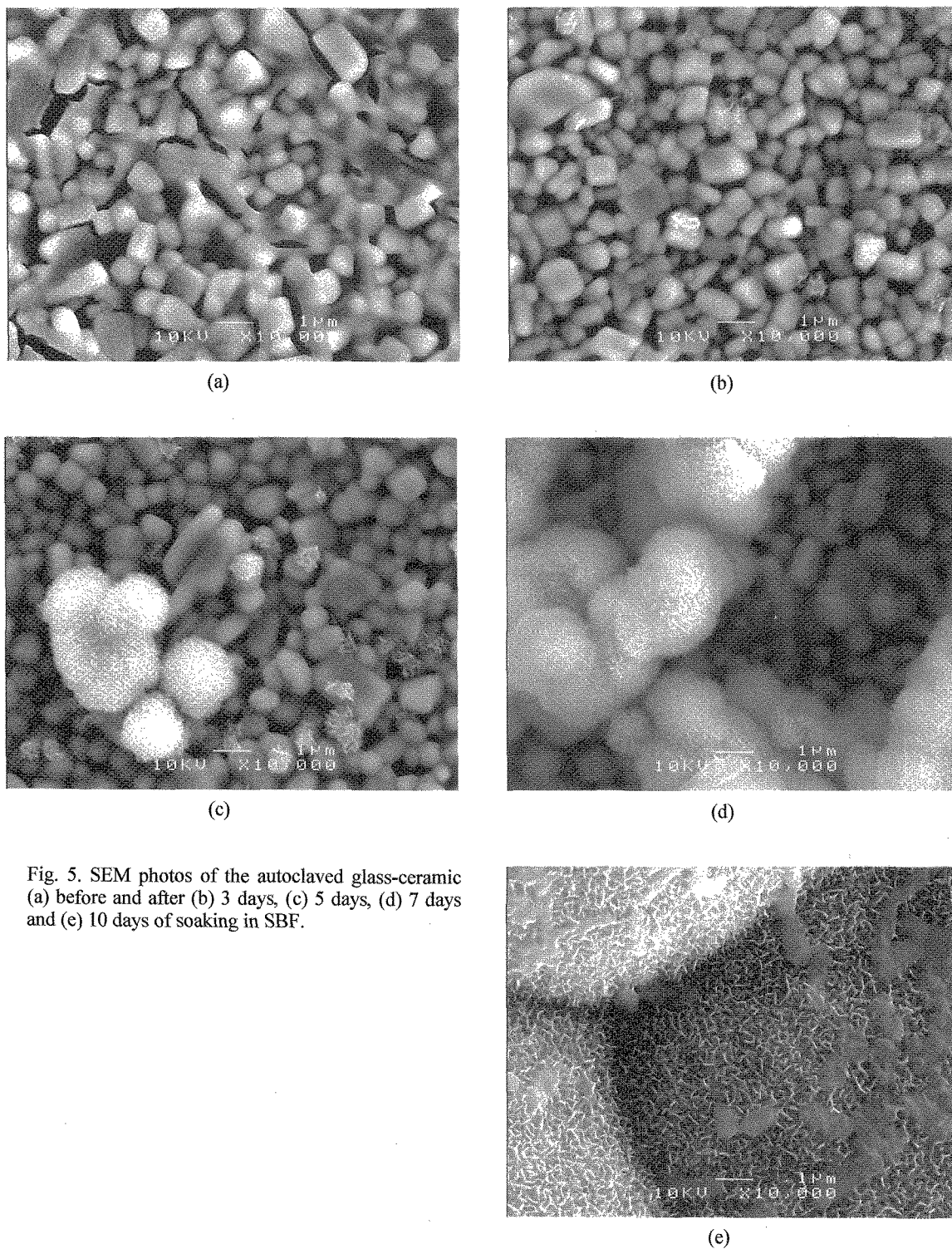


Fig. 5. SEM photos of the autoclaved glass-ceramic (a) before and after (b) 3 days, (c) 5 days, (d) 7 days and (e) 10 days of soaking in SBF.

and 465.5 eV disappeared and the peaks newly appeared at 458.5 eV and 464.2 eV, which are close to those from a Ti-O bonding in TiO₂ crystal.¹⁶ Fig. 6 shows laser Raman spectra before and after the autoclaving. Almost no changes in the spectra are seen except appearance of a peak at ~145 cm⁻¹ after the autoclaving. The peak is suggested to be due to TiO₂ crystal (anatase phase)¹⁷. That is, it is suggested that bondings around titanium ions in the amorphous phases are broken to newly form an anatase phase at the surface during the autoclaving. It was reported that anatase crystal plays an important role in apatite formation in SBF.¹⁸

Two kinds of calcium phosphate ceramics such as β-CPP and β-TCP were prepared by sintering the compacts of the commercial powders (Taihei Chemical Industrial Co. Ltd.) at 1000 °C and 1070 °C, respectively, for 3 h, and they were autoclaved at 140 °C for 1 h in water as well as the glass-ceramic. When the autoclaved samples were soaked in SBF for 10 days, no apatite formed on β-CPP ceramic, while the bonelike apatite started to form on β-TCP. The glass-ceramic was completely covered with the apatite after 10 days of soaking. This result may imply that the apatite formation is strongly influenced by the chemical change in the amorphous titania phase around the surface of the glass-ceramic.

The composition of the autoclaved glass-ceramic surface was estimated from the EDS spectrum to be Ca:P:Na:Ti = 52:43:3:2 in cationic percentage. In comparison with the nominal composition (Ca:P:Na:Ti = 44:44:10:2) of the glass-ceramic, the calcium amount is larger, and the sodium and phosphorus amounts are

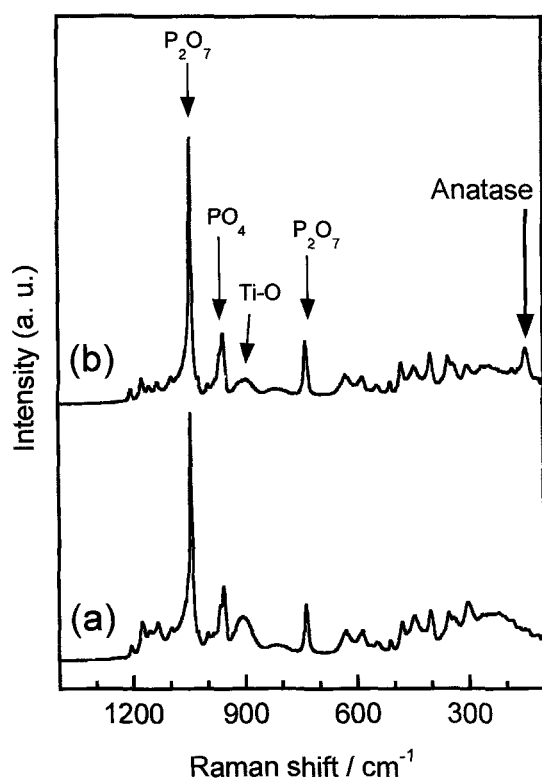


Fig. 6. Laser Raman spectra of the glass-ceramics (a) before and (b) after autoclaving.

slightly smaller; there is almost no change in the titanium amount. This result implies that the phosphate glassy phase around the surface dissolves drastically during the autoclaving; sodium, calcium and phosphorus ions dissolve. The initial pH value of the water used for the autoclaving was measured to be ~6.0, and, after the treatment, the final value was done to be ~6.8. Almost no titanium ions would dissolve into the water at pH 6-7 and the ions may form the hydrated group containing Ti-OH around the surface. When the autoclaved sample is soaked in SBF, the negative-charged, hydrated titania groups and anatase crystals around the surface would induce nucleation of the apatite. As a result, the apatite forms after the soaking in a short period.

4. SUMMARY

Calcium pyrophosphate glass-ceramic with easy machinability was prepared by heating a compact of glass powders with a composition of 60CaO-30P₂O₅-7Na₂O-3TiO₂ at 850 °C. The glass-ceramic contains a large amount of β-calcium pyrophosphate crystal with a β-tricalcium phosphate crystal in the glassy matrix phase. The machinability is attributed to the microstructure consisting of interlocking the pyrophosphate crystals in which plate-like products with thickness of several tens nanometers are piled up. It shows a relatively high bending strength of 100-120 MPa. When the glass-ceramic was autoclaved in water prior to the soaking in SBF, bonelike apatite started to form on the autoclaved glass-ceramic after 3 days of soaking in SBF at 37 °C. The surface was completely covered with the apatite after 10 days of soaking; the apatite-forming ability could be drastically improved after autoclaving in water in comparison with that of non-treated sample. Although the residual glassy phase around the surface dissolved during the autoclaving in water, titanium ion in the phase stayed around the surface. XPS and laser Raman spectroscopic analysis suggested that anatase crystals and hydrated titania groups form newly around the surface during the autoclaving. The surface modification is suggested to enhance the apatite-forming ability.

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