EFFECTS OF VARIOUS METAL-OXIDE ADDITIONS ON SINTERING OF 
β-CALCIUM ORTHOPHOSPHATE PREPARED BY SPRAY-PYROLYSIS

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Abstract Effects of various metal-oxide additions on sintering of β-calcium orthophosphate (β-Ca$_3$(PO$_4$)$_2$) were examined. The metal-oxide additives used in this experiment were: (i) the monovalent metal oxides Li$_2$O, Na$_2$O and K$_2$O; (ii) the divalent metal oxides MgO, CaO, SrO and BaO; (iii) trivalent metal oxides Al$_2$O$_3$ and Fe$_2$O$_3$; (iv) tetravalent metal oxides SiO$_2$, TiO$_2$ and ZrO$_2$. The sintering of β-Ca$_3$(PO$_4$)$_2$ was promoted only by the addition of Fe$_2$O$_3$; the relative density of the sintered compact with 10 mol% of Fe$_2$O$_3$ addition fired at 1070°C for 5 h attained 98.7%.

INTRODUCTION

The calcium orthophosphate (β-Ca$_3$(PO$_4$)$_2$) ceramics may be applicable to the bone and tooth implant materials. Since the mechanical strengths of such ceramics are required to be high enough for the practical uses, our attention has been directed toward the fabrication of the dense β-Ca$_3$(PO$_4$)$_2$ ceramics, using the easily-sinterable β-Ca$_3$(PO$_4$)$_2$ powder prepared by spray pyrolysis; the relative density of the powder compact fired at 1070°C for 5 h attained 96.1%. More information on the effects of metal-oxide additions on sintering of β-Ca$_3$(PO$_4$)$_2$ is needed to fabricate the dense β-Ca$_3$(PO$_4$)$_2$ ceramics. Although the effects of some additives on sintering of β-Ca$_3$(PO$_4$)$_2$ have been conducted by Toriyama et al., no systematical investigation has been carried out so far. This paper describes the effects of various metal-oxide additions on sintering of β-Ca$_3$(PO$_4$)$_2$.

EXPERIMENTAL PROCEDURES

The starting β-Ca$_3$(PO$_4$)$_2$ powder was prepared by spray-pyrolyzing the mixed solutions of 0.9 mol·dm$^{-3}$ Ca(NO$_3$)$_2$ and 0.6 mol·dm$^{-3}$ (NH$_4$)$_2$HPO$_4$ at 600°C, using an air-liquid nozzle. The spray-pyrolysed powder was heated at 600°C for 1 h and then was
pulverized using the grinding apparatus (Model AGA, Ishikawa Kojo MFG). All of the additives were commercially available metal oxides and carbonates: (i) the monovalent metal carbonates Li$_2$CO$_3$ and Na$_2$CO$_3$ and K$_2$CO$_3$; (ii) the divalent metal oxide and carbonates MgO, CaCO$_3$, BaCO$_3$ and SrCO$_3$; (iii) trivalent metal oxides Al$_2$O$_3$ and Fe$_2$O$_3$; (iv) tetravalent metal oxides SiO$_2$, TiO$_2$ and ZrO$_2$.

The $\beta$-Ca$_3$(PO$_4$)$_2$ powder was mixed with the desired amount of metal oxide or carbonate in the presence of acetone and was uniaxially pressed at 30 MPa to form a cylindrical compact with a diameter of 20 mm and a thickness of ~2 mm. The compact was heated at the rate of 10°C·min$^{-1}$ and was held at 1070°C for 5 h in air. The bulk densities of the green and sintered compacts were measured on the basis of the weights and dimensions. The relative density of the sintered compact was calculated by dividing the bulk density by the true density measured picnometrically at 25°C.

The crystalline phases of the sintered compact were examined using an X-ray diffractometer (XRD; Model RAD-IIA, Rigaku; 40 kV, 25 mA) with Ni-filtered CuK $\alpha$ radiation. The microstructure of the sintered compact was observed using a scanning electron microscope (SEM: Model S-4500, Hitachi).

RESULTS AND DISCUSSION

The crystalline phases and relative densities of the compacts with metal-oxide additions fired at 1070°C for 5 h are listed in Table 1, together with the ionic radii of the cations. These properties are discussed below:

(1) Crystalline phases of the sintered compacts

The crystalline phases of the sintered compacts with monovalent and divalent metal oxide additions were $\beta$-Ca$_3$(PO$_4$)$_2$ and the reaction product identified as hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$; HAp), except for the case of the sintered compact with BaO addition where $\alpha$-Ca$_3$(PO$_4$)$_2$ and HAp were present. The HAp may be formed via (i) thermal decomposition of $\beta$-Ca$_3$(PO$_4$)$_2$ in the presence of the metal oxides and (ii) the reaction of Ca$_{10}$(PO$_4$)$_6$O with water vapor in air during cooling. The fact that the sintered compact with BaO addition contained $\alpha$-Ca$_3$(PO$_4$)$_2$ suggests that the transformation temperature of $\beta$-Ca$_3$(PO$_4$)$_2$ to $\alpha$-Ca$_3$(PO$_4$)$_2$ may be lowered down by the addition of BaO.$^2$
Relative densities of the sintered compacts

Most of the relative densities of the sintered compacts with metal-oxide additions were lower than the density (96.1%) of the pure sintered $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ compact; however, the relative density of the sintered compact with $\text{Fe}_2\text{O}_3$ addition attained 98.7%. We also examined the effect of the amount of metal oxide on sintering of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$. Typical results of the sintered compact with $\text{Fe}_2\text{O}_3$ addition are shown in Fig. 1. The relative density of the sintered compact increased with $\text{Fe}_2\text{O}_3$ addition. In order to check whether the sintering of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ was promoted by the solid solution of $\text{Fe}_2\text{O}_3$ into $\beta$-$\text{Ca}_3(\text{PO}_4)_2$, we measured the lattice constants of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$. Results are shown in Fig. 2. The a-axis and c-axis lengths were 1.043 and 3.738 nm, respectively. Since these lattice constants are almost in accord with those of pure $\beta$-$\text{Ca}_3(\text{PO}_4)_2$, no solid solution of $\text{Fe}_2\text{O}_3$

### Table 1  The crystalline phases and relative densities of the compacts with 10 mol% of metal-oxide additions fired at 1070°C for 5 h.

<table>
<thead>
<tr>
<th>Valence</th>
<th>Metal oxide</th>
<th>Ionic radius</th>
<th>Crystalline phase</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>Li$_2$O</td>
<td>0.060</td>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$, Hydroxypatite</td>
<td>84.7</td>
</tr>
<tr>
<td>+1</td>
<td>Na$_2$O</td>
<td>0.095</td>
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<tr>
<td>+1</td>
<td>K$_2$O</td>
<td>0.133</td>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$, Hydroxypatite</td>
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<tr>
<td>+2</td>
<td>MgO</td>
<td>0.065</td>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$, Hydroxypatite</td>
<td>89.6</td>
</tr>
<tr>
<td>+2</td>
<td>CaO</td>
<td>0.099</td>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$, Hydroxypatite</td>
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<td>+2</td>
<td>SrO</td>
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<tr>
<td>+2</td>
<td>BaO</td>
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<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$</td>
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<tr>
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<tr>
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<td>TiO$_2$</td>
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<tr>
<td>+4</td>
<td>ZrO$_2$</td>
<td>0.080</td>
<td>$\beta$-$\text{Ca}_3(\text{PO}_4)_2$, ZrO$_2$</td>
<td>92.1</td>
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</table>

a) Identified by X-ray diffractometry.

(2) Relative densities of the sintered compacts

Most of the relative densities of the sintered compacts with metal-oxide additions were lower than the density (96.1%) of the pure sintered $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ compact; however, the relative density of the sintered compact with $\text{Fe}_2\text{O}_3$ addition attained 98.7%. We also examined the effect of the amount of metal oxide on sintering of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$. Typical results of the sintered compact with $\text{Fe}_2\text{O}_3$ addition are shown in Fig. 1. The relative density of the sintered compact increased with $\text{Fe}_2\text{O}_3$ addition. In order to check whether the sintering of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$ was promoted by the solid solution of $\text{Fe}_2\text{O}_3$ into $\beta$-$\text{Ca}_3(\text{PO}_4)_2$, we measured the lattice constants of $\beta$-$\text{Ca}_3(\text{PO}_4)_2$. Results are shown in Fig. 2. The a-axis and c-axis lengths were 1.043 and 3.738 nm, respectively. Since these lattice constants are almost in accord with those of pure $\beta$-$\text{Ca}_3(\text{PO}_4)_2$, no solid solution of $\text{Fe}_2\text{O}_3$
into β-Ca₃(PO₄)₂ seems to occur. We consider that β-Ca₃(PO₄)₂ may react with Fe₂O₃ to form the liquid phase(s) in the 2Fe₂O₃•P₂O₅-Fe₂O₃•P₂O₅ system and/or Fe₂O₃•P₂O₅ - 2Fe₂O₃•3P₂O₅ system above 950°C, thus the densification would be promoted. The SEM micrograph of this sintered compact showed that the spherical grains with diameters of ~2 µm were closely packed. The presence of such spherical grains demonstrates the formation of the liquid phases during firing.

**CONCLUSION**

The effects of various metal oxide additions on sintering of β-Ca₃(PO₄)₂ were examined. The metal-oxide additives used were: (i) the monovalent metal oxides Li₂O and Na₂O and K₂O; (ii) the divalent metal oxides MgO, CaO, BaO and SrO; trivalent metal oxides Al₂O₃ and Fe₂O₃; (iv) tetravalent metal oxides SiO₂ and ZrO₂. Most of the relative densities of the compacts with 10 mol% of metal-oxide additions fired at 1070°C for 5 h were lower than the density (96.1%) of pure β-Ca₃(PO₄)₂ compact. The sintering of β-Ca₃(PO₄)₂ was promoted only by the addition of Fe₂O₃, due to the presence of the liquid phase during firing. The relative density of the sintered β-Ca₃(PO₄)₂ compact with Fe₂O₃ addition attained 98.7%.

**REFERENCES**