

Bioactivity of Nb(V) and Ta(V)-Doped Calcium Silicate Glasses

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Nb₂O₅- and Ta₂O₅-doped calcium silicate glasses were soaked for various periods in a simulated body fluid (Kokubo solution) up to 30 days. Apatite formation ability of the surface of these glasses were investigated with thin-film X-ray diffraction and FT-IR reflection spectroscopy. The effects of these additive oxides on the bioactivity of CaO•SiO₂ based glass were discussed. A small amount of Nb₂O₅ and Ta₂O₅ suppressed the rate of silica hydrogel layer formation and the apatite formation on the surface of the glasses. The rate of the apatite nucleation on the surface of Nb₂O₅-doped calcium silicate glass was slower than that on the surface of Ta₂O₅-doped calcium silicate glass. It was concluded that the decrease in the apatite forming ability of calcium silicate glasses by these additive oxides is attributed to the suppression of formation of silica hydrogel layer which plays an important role in apatite nucleation.

1. INTRODUCTION

The essential condition for glasses and glass-ceramics to bond to living bone is the formation of a biologically active bone-like apatite layer on their surfaces when they are embedded in human body. A few series of several glasses and glass-ceramics containing CaO and SiO₂ such as Ceravital^{®1)} and Cerabone^{® A-W²⁾} have exhibited bioactivity. The 50CaO•50SiO₂ glass is important for its good bioactivity and has been well studied^{3,4)}. Ohtsuki *et al.*⁹⁾ have already suggested that the dissolution of Ca(II) and Si(IV) ions from 50CaO•50SiO₂ glass and the silica hydrogel layer formed on the surface of the glass plays an important role in apatite nucleation. However, it has been shown that the addition of the third component such as TiO₂ and Al₂O₃ depressed the bioactivity⁵⁾, while the addition of B₂O₃ results in better bioactivity⁶⁾. Thus, those cations causes opposite effects on the bioactivity depending on their content as they modified the chemical properties of the glass. Recently, we have found that not only silica hydrogel (Si(IV)) and titania hydrogel (Ti(IV)) but also multivalent Ta(V) species play an important role in an apatite formation⁷⁾. We can expect that the incorporation of multivalent cations such as Nb(V) and Ta(V) in the CaO•SiO₂ based glass also changes its bioactivity and the mechanism of apatite formation as well as its chemical properties. It was worth examining the effect of the incorporation of multivalent cations on bioactivity.

In the present study, in order to investigate fundamentally the effect of addition of Nb(V) and Ta(V) on the bioactivity of CaO•SiO₂ based glasses, the compositional dependence of apatite formation on the surface of glasses in the system xNb₂O₅•(50-x/2)CaO•(50-x/2)SiO₂ and xTa₂O₅•(50-x/2)CaO•(50-x/2)SiO₂ (x=1, 2 and 5 mol%) was examined in the simulated body fluid.

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2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Nb₂O₅- and Ta₂O₅-Doped Calcium Silicate Glasses

$x\text{Nb}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ and $x\text{Ta}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ($x=1, 2$ and 5 mol%) glasses were prepared. Starting materials were reagent grade SiO_2 , CaCO_3 , Nb_2O_5 and Ta_2O_5 chemicals supplied by Nacalai Tesque, Inc. The appropriate amounts of the starting materials were mixed and melted with a 30ml platinum crucible placed in a MoSi_2 electric furnace at 1600°C for an hour. The melts were poured onto a steel plate and immediately pressed with another one to be formed into a plate about 1mm thick, and allowed to cool in an SiC furnace from 700°C . Rectangular specimens of $15 \times 10 \times 1 \text{ mm}^3$ were cut from the obtained glass. Both surfaces of the specimens were polished with a diamond paste (1mm in diameter) and washed with acetone in an ultrasonic cleaner.

2.2. Soaking in SBF

The obtained specimens were soaked in 35ml of a simulated body fluid (SBF; Kokubo solution) kept at 36.5°C , which had inorganic species similar in concentration to those of the human blood plasma. The fluid was prepared by dissolving reagent grade chemicals of NaCl , NaHCO_3 , KCl , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 and Na_2SO_4 in distilled water as described elsewhere⁹. It was buffered at pH 7.25 with 50mM trishydroxymethylaminomethane ($(\text{CH}_2\text{OH})_3\text{CNH}_2$) and 45mM HCl, and its temperature was kept at 36.5°C . SBF is already confirmed to be able to well reproduce the apatite formation on the surfaces of glasses and glass-ceramics in the body environment.

2.3. Analysis of Surface Structure

After soaking in the SBF for various periods, specimen was removed from the fluid and gently washed with acetone. The surface structure was examined with thin-film X-ray diffraction and Fourier-transform infrared (FT-IR) reflection spectroscopy. An X-ray diffraction attached with a thin-film attachment was used, and the glancing angle was fixed at 1° , while an infrared spectrometer (FT-IR 300, Jasco Co., Japan) was used, and the reflection angle to the normal was set at 75° . Both techniques enabled to detect a layer about $1 \mu\text{m}$ thick at the surface of the specimen.

2.4. Measurement of Element Concentration

After the specimen was removed from the SBF, the concentration of calcium, silicon and phosphorus in the SBF were measured with an inductively coupled plasma (ICP) emission spectroscopy. pH of the fluids was also measured.

3. RESULTS AND DISCUSSION

Figure 1 shows that thin-film X-ray diffraction patterns and FT-IR reflection spectra of the surface of $50\text{CaO} \cdot 50\text{SiO}_2$ glasses before and after soaking up to 30 days in the SBF. The X-ray diffraction patterns and FT-IR reflection spectra for a specimen without soaking are denoted as "0d". The main peaks in Fig. 1 were assigned to as described on the basis of the data previously reported^{3,4}. It can be seen from Fig. 1 that $50\text{CaO} \cdot 50\text{SiO}_2$ glass

forms an apatite phase (X-ray diffraction near 26° and 32°) on their surfaces in the SBF in 1 day. The IR reflection peaks at 500 , 650 , 1100 and 1250 cm^{-1} were ascribed to Si-O bending vibration, P-O bending vibration, transverse optical mode of Si-O stretching vibration and longitudinal optical mode of Si-O stretching vibration, respectively.

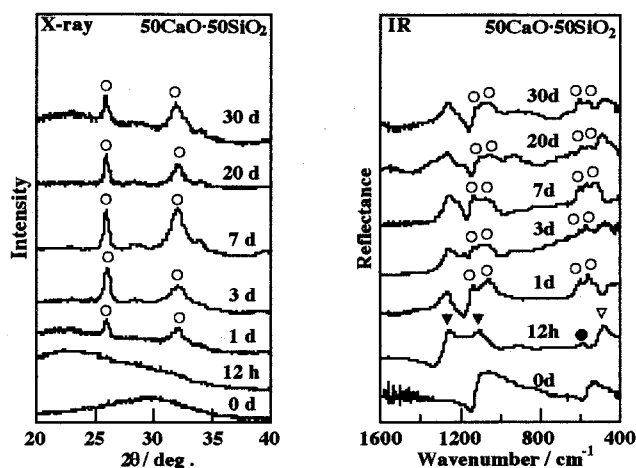


Fig. 1 Thin-film X-ray diffraction patterns and FT-IR reflection spectra of the surface of $50\text{CaO}\cdot 50\text{SiO}_2$ glasses before and after soaking up to 30 days in the SBF.

The IR reflection peaks at 1100 and 1250 cm^{-1} appeared after 12 hours and grew in intensity and the relative intensity of the 1100 and 1250 cm^{-1} peaks decreased with increasing soaking periods. This indicates that these glasses form a silica hydrogel layer on their surfaces. The 1130 cm^{-1} peak due to apatite was observed after immersion for 1 day.

Figure 2 shows changes in element concentration of the SBF due to the immersion of $50\text{CaO}\cdot 50\text{SiO}_2$ glass. It can be seen that the calcium and silicon concentrations increase and the phosphorus concentration decreases with soaking periods. The calcium and silicon concentrations increase for the glass soaked in the SBF until 12 hours. The increase in calcium and silicon concentrations is due to dissolution of $\text{Ca}(\text{II})$ and $\text{Si}(\text{IV})$ ions from the glass. After immersion for 1 day the calcium and phosphorus concentrations decreased. This indicates that the apatite nuclei were formed on the surfaces of the $50\text{CaO}\cdot 50\text{SiO}_2$ glass until 12 hours and grew by consuming the calcium and phosphorous ions from the SBF.

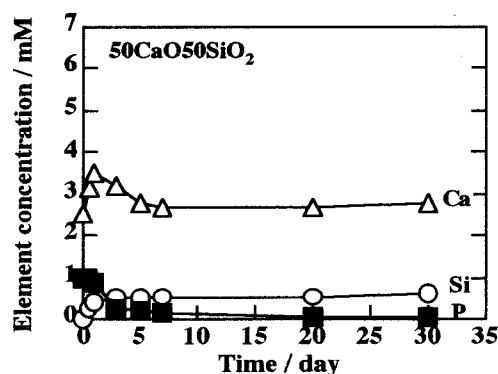


Fig. 2 Changes in element concentrations due to immersion of $50\text{CaO}\cdot 50\text{SiO}_2$ glass.

Figure 3(a), (b) and (c) show that thin-film X-ray diffraction patterns and FT-IR reflection spectra of the surface of the $x\text{Nb}_2\text{O}_5\cdot (50-x/2)\text{CaO}\cdot (50-x/2)\text{SiO}_2$ ($x=1, 2$ and 5 mol%) glasses before and after soaking up to 30 days in the SBF. The main peaks in Fig. 3 were assigned to as described on the basis of the data previously reported^(3,4). It can be seen from Fig. 3(a), (b) and (c) that only $1\text{Nb}_2\text{O}_5\cdot 49.5\text{CaO}\cdot 49.5\text{SiO}_2$ glass forms an apatite phase (X-ray diffraction near 26° and 32°) on their surfaces in the SBF in 30 days, while other glasses do not form it. When $x=5$ in the $x\text{Nb}_2\text{O}_5\cdot (50-x/2)\text{CaO}\cdot (50-x/2)\text{SiO}_2$ glass, the spectral profile did not change after soaking. On the other hand, when $x=1$ and 2 , the IR reflection peaks at 1150 and 1250 cm^{-1} appeared after 1 day and grew in intensity and the relative intensity of the 1150 and 1250 cm^{-1} peaks decreased with increasing soaking periods. This indicates that these glasses form a silica hydrogel layer on their surfaces. In $1\text{Nb}_2\text{O}_5\cdot 49.5\text{CaO}\cdot 49.5\text{SiO}_2$ the 1130 cm^{-1} peak due to apatite was observed after immersion for 30 days. In the $5\text{Nb}_2\text{O}_5\cdot 47.5\text{CaO}\cdot 47.5\text{SiO}_2$ glass the spectral profile did not change after soaking. Figure 3(d), (e) and (f) show that thin-film X-ray diffraction patterns

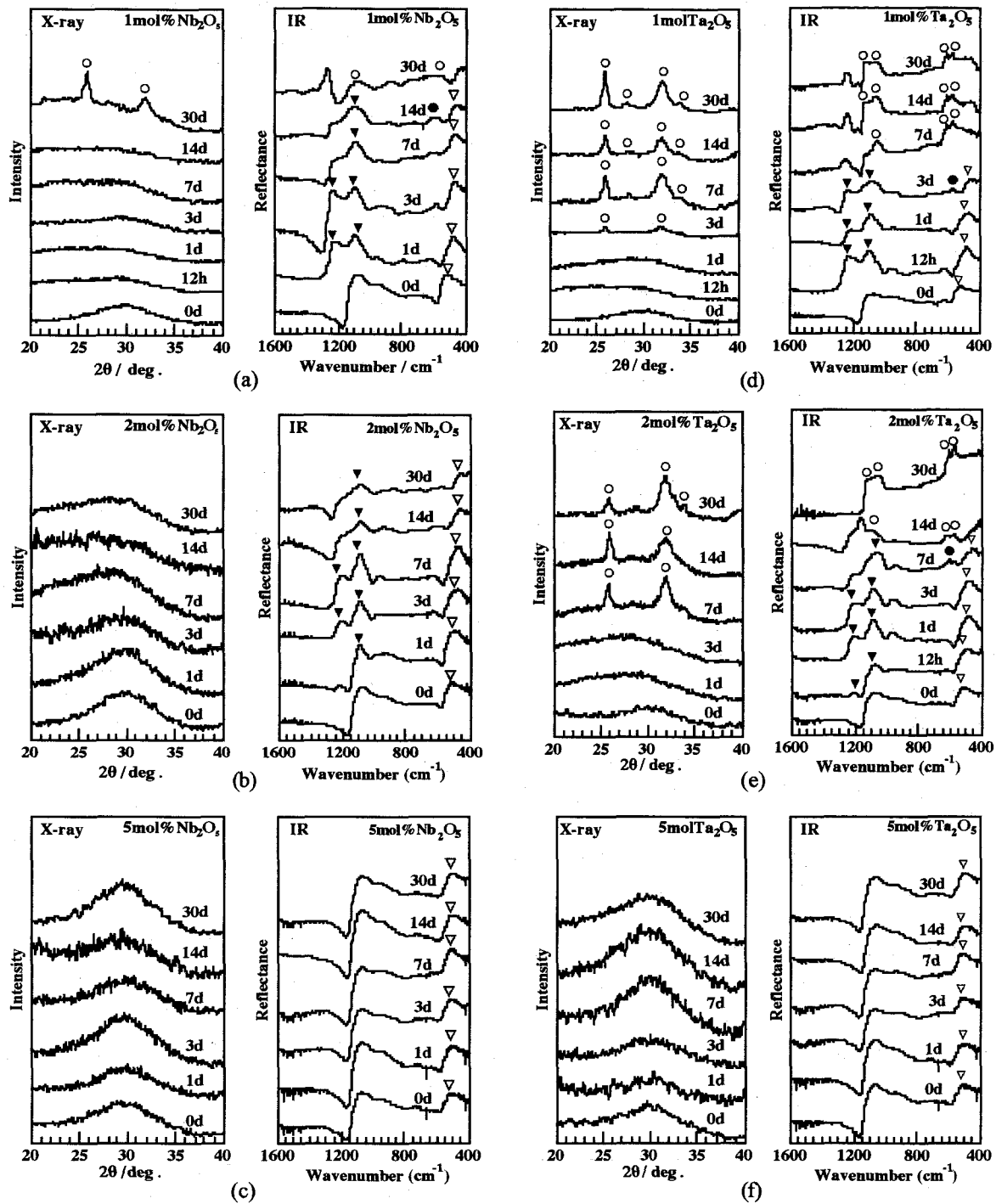


Fig. 3 Thin-film X-ray diffraction patterns and FT-IR reflection spectra of the surface of the $x\text{Nb}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ((a) $x=1$, (b) $x=2$ and (c) $x=5$ mol%) and $x\text{Ta}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ((d) $x=1$, (e) $x=2$ and (f) $x=5$ mol%) glasses before and after soaking up to 30 days in the SBF.

and FT-IR reflection spectra of the surface of $x\text{Ta}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ($x=1, 2$ and 5 mol%) glasses before and after soaking up to 30 days in the SBF. It can be seen from Fig. 3(d) and (e) that $x\text{Ta}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ($x=1$ and 2 mol%) glasses form an apatite phase on their surfaces in the SBF in 3 and 7 days, respectively, while $5\text{Ta}_2\text{O}_5 \cdot 47.5\text{CaO} \cdot 47.5\text{SiO}_2$ glass does not form it. In the $5\text{Ta}_2\text{O}_5 \cdot 47.5\text{CaO} \cdot 47.5\text{SiO}_2$ glass the spectral profile did not change after soaking. On the other hand, when $x=1$ and 2 , the IR reflection peaks at 1100 and 1250 cm^{-1} appeared after 12h. This indicates that these glass forms silica hydrogel layer on their surfaces. In the $1\text{Ta}_2\text{O}_5 \cdot 49.5\text{CaO} \cdot 49.5\text{SiO}_2$ and $2\text{Ta}_2\text{O}_5 \cdot 49\text{CaO} \cdot 49\text{SiO}_2$ glasses the 540 cm^{-1} peak grew and finally split into two peaks at 570 and 610 cm^{-1} due to apatite after 7 days. In the $2\text{Ta}_2\text{O}_5 \cdot 49\text{CaO} \cdot 49\text{SiO}_2$ glass the 540 cm^{-1} peak grew and finally split into two peaks at 570 and 610 cm^{-1} due to apatite after 14 days.

Figure 4(a), (b) and (c) show changes in element concentration of the SBF due to the immersion of the $x\text{Nb}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ($x=1, 2$ and 5 mol%) glasses. It can be seen from Fig. 4(a) and (b) that the calcium and silicon concentration increase and the phosphorus concentration decreases with soaking periods. The increase in calcium and silicon concentrations is due to dissolution of Ca(II) and Si(IV) ions from the glass. Figure 4(d), (e) and (f) show changes in element concentration of the SBF due to the immersion of the $x\text{Ta}_2\text{O}_5 \cdot (50-x/2)\text{CaO} \cdot (50-x/2)\text{SiO}_2$ ($x=1, 2$ and 5 mol%) glasses. It can be seen that the calcium concentration increases for the glass soaked in the SBF until 3 days. After immersion for 3 days the calcium and phosphorus concentrations

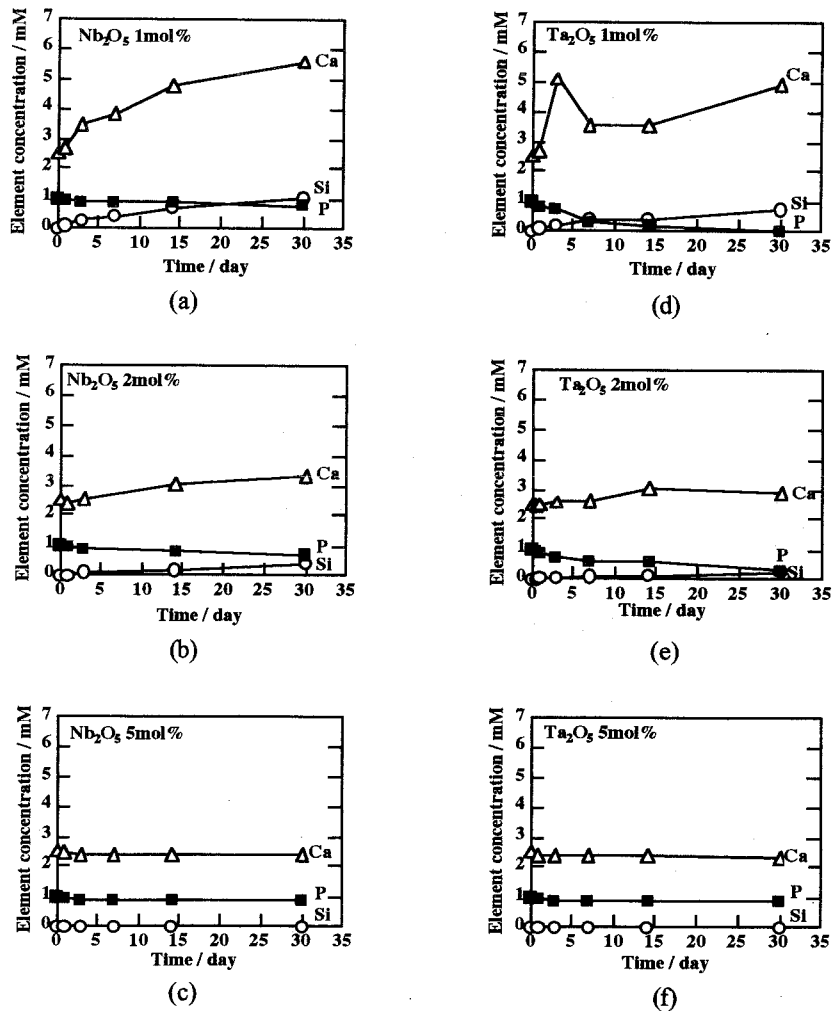


Fig. 4 Changes in element concentrations due to immersion of Nb_2O_5 - and Ta_2O_5 -doped calcium silicate glasses.

decreased. This indicates that the apatite nuclei were formed on the surfaces of the $1\text{Ta}_2\text{O}_5 \cdot 49.5\text{CaO} \cdot 49.5\text{SiO}_2$ glass until 3 days and grow by consuming the calcium and phosphorous ions from the SBF. Figure 2(e) and (f) show that the calcium and phosphorus concentration decrease with soaking periods and the silicon concentration is not be detected. The rate of dissolution of Ca(II) and Si(IV) ions decreases with increasing Nb_2O_5 and Ta_2O_5 content. The change in element concentration due to immersion of Nb_2O_5 -doped glasses were similar to that of Ta_2O_5 -doped glasses. The present results indicates that the incorporation of Nb_2O_5 and Ta_2O_5 in $\text{CaO} \cdot \text{SiO}_2$ based glass suppressed the formation of silica hydrogel layer which plays an important role in apatite nucleation.

4. SUMMARY

We examined the apatite formation on the surface of Nb_2O_5 - and Ta_2O_5 -doped calcium silicate glasses in order to investigate fundamentally the effect of addition of Nb(V) and Ta(V) on the bioactivity of $\text{CaO} \cdot \text{SiO}_2$ based glasses. Nb_2O_5 - and Ta_2O_5 -doped calcium silicate glasses were soaked for various periods in a simulated body fluid(Kokubo solution) up to 30 days. A small amount of additive oxides, Nb_2O_5 and Ta_2O_5 , suppressed the rate of silica hydrogel layer formation and the apatite formation on the surface of the glasses. The rate of the apatite nucleation on the surface of Nb_2O_5 -doped calcium silicate glass was slower than that on the surface of Ta_2O_5 -doped calcium silicate glass. The decrease in the apatite forming ability of calcium silicate glasses by these additive oxides is attributed to the suppression of formation of silica hydrogel layer which plays an important role in apatite nucleation.

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