Structures and dissolution behaviors of CaO-P2O5-TiO2-Nb2O5 (Ca/P = 1) invert glasses

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Structures and dissolution behaviors of CaO-P$_2$O$_5$-TiO$_2$/Nb$_2$O$_5$ (Ca/P ≥ 1) invert glasses

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Abstract

Common phosphate glasses—for example, those in the metaphosphate region—show potential as biodegradable materials. Some applications, such as biocompatible thin films coated on titanium or its alloys using radiofrequency magnetron sputtering methods, require films with good chemical durability. In the present work, CaO-P$_2$O$_5$-TiO$_2$/Nb$_2$O$_5$ glasses with a Ca/P ratio of $\geq 1.00$ were prepared using a melt-quenching method, and their structures and dissolution behaviors were investigated. When the Ca/P ratio was increased, the amount of orthophosphate (Q$_p^0$) group in the glasses increased, and that of pyrophosphate (Q$_p^1$) group decreased. The amount of Q$_p^0$ group was greater than the amount of Q$_p^1$ groups in glasses with a Ca/P ratio of $\geq 1.14$. Intermediate oxides (i.e., TiO$_2$ and Nb$_2$O$_5$) in the glasses cross-linked with the phosphate groups to form P-O-Ti/Nb bonds; these bonds were expected to take a tetrahedral form. The glasses prepared in the present work showed excellent chemical durability, because of the P-O-Ti/Nb bonds and the delocalized P=O bonds that resulted from the increasing Q$_p^0$ content in the glasses.
1 Highlights

2 • Phosphate glasses including numerous orthophosphate groups (\(Q_p^0\)) were prepared
3 • The number of P-O-Ti/Nb bonds increased with increasing \(Q_p^0\) content in the glasses
4 • TiO\(_x\)/NbO\(_y\) groups formed tetrahedrons in the glasses including numerous \(Q_p^0\) groups
5 • The chemical durability increased with increasing \(Q_p^0\) content in the glasses

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10 Keywords

11 Biomaterial, calcium phosphate glass, invert glass, structure, dissolution
1. Introduction

Titanium-containing calcium phosphate invert glasses (Ti-IGs) have been a focus of research in our group [1]. Ti-IGs consist of short phosphate groups, such as ortho- and pyrophosphates ($Q^0_p$ and $Q^1_p$), because P-O-Ti bonds help to form their glass network [1]. Ti-IGs indicate in vitro and in vivo bioactivity [2,3]. Ti-IGs can be applied as a coating material for titanium or its alloys. In our previous work, Ti-IG powders were dip coated on a Ti-29Nb-13Ta-4.6Zr alloy, and then heat treated at 800°C for 1 h. The resulting layer were 10 ~ 20 μm in thickness, without significant cracks, and the tensile bonding strength between the layer and the substrate was measured to be 26 MPa [4]. Recently, niobium-containing calcium phosphate invert glasses (Nb-IGs) were prepared by our group [5,6]. Crystallized Nb-IGs showed apatite-forming abilities in simulated body fluids [5]. Trace amounts of Nb$^{5+}$ ions (0.04 ~ 0.06 mM) dissolved from the Nb-IGs enhanced the differentiation of osteoblast-like cells, such as alkali phosphatase (ALP) activity [6]. Tamai et al. reported that Nb$^{5+}$ ions enhanced calcification, because of the enhancement of the ALP activity [7]. Narushima et al. reported an amorphous calcium phosphate film prepared on metallic titanium using a radiofrequency magnetron sputtering (RF-sputtering) method [8]. The tensile strength of the bond between the film and the titanium was greater than
60 MPa when the coating layer thickness was between 0.5 and 1 μm (the epoxy glue used in the test was detached without damage to the film) [9]. The bonding strength decreased to 30 MPa after the amorphous calcium phosphate film on the titanium was immersed in phosphate-buffered saline (PBS) for 3 days, because of the low chemical durability of the film [10]. Amorphous films on metallic titanium or its alloys are required to have excellent chemical durability and excellent biocompatibility.

Ti-IGs and Nb-IGs may be candidate for the amorphous film using RF-sputtering method. To fully realize the application of method for Ti-IGs and Nb-IGs, it is necessary to clarify their (Ti-IGs and Nb-IGs) dissolution behaviors. In this work, we focused on phosphate invert glasses containing TiO₂ or Nb₂O₅ and large amounts of CaO (where the invert glasses were prepared via conventional melt-quenching), and examined their structures and dissolution behaviors.

2. Materials and methods

2.1 Preparation of the glasses

Titanium- or niobium-containing calcium phosphate invert glasses with nominal compositions of xCaO(90-x)P₂O₅·10TiO₂ (mol%, x = 60 to 66, denoted here as Ti-IGs)
and $y\text{CaO} \cdot (94.5-y)\text{P}_2\text{O}_5 \cdot 5.5\text{Nb}_2\text{O}_5$ (mol%, $y = 63$ to 68.5, denoted here as Nb-IGs) were prepared, as shown in Table 1. Glass batches were prepared using CaCO$_3$ (99.5%), H$_3$PO$_4$ (85% liquid), TiO$_2$ (99.5%), and Nb$_2$O$_5$ (99.9%). All reagents were obtained from Kishida Chemical Co., Japan. The glass compositions were adjusted by changing the atomic ratios of Ca, P, and Ti or Nb. The reagents were mixed with distilled water to make a slurry at room temperature. After the mixture was dried under an infrared lamp overnight and then stored at 140°C, it was melted in a platinum crucible at 1500°C for 30 min, and then quenched via pressing, which was applied using two stainless-steel plates, to prevent crystallization. The resulting glass compositions were examined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-7000, Shimadzu Co., Japan) for the Ti-IGs, using aqueous solutions in which 5 mg of the glass powders was dissolved in 20 mL of 1N HCl ($n = 3$). The compositions of the Nb-IGs were analyzed using energy dispersive X-ray spectroscopy (EDX, JCM-6000 and JED-2300, JEOL Co., Japan): the glass fractures were coated with amorphous osmium using plasma chemical vapor deposition equipment ($n = 3$).

### 2.2 Thermal analysis

The glass transition temperature ($T_g$) and crystallization temperature ($T_c$, defined
as the onset of crystallization) of the glasses were obtained using differential thermal
analysis (DTA; heating rate: 5 K/min, Thermo plus TG8120, Rigaku Co., Japan). The
glassification degree—which is defined as $(T_c - T_g)/T_g$ (K/K) [11], and is used as an
indicator of the glass-forming ability—was calculated.

2.3 Characterization of the glass structure

The glass structure was investigated using laser Raman spectroscopy, which was
performed on quenched glass samples in the Raman shift region between 500 and 1300

cm$^{-1}$ (NRS-3300, JASCO Co., Japan). The samples were excited by the 532.08 nm line

of Nd:YAG solid-state laser with 6.4 mW of power at room temperature. The exposure
time was 10 sec and the cumulated number was 8. The resolution of Raman spectra is

4.13 cm$^{-1}$.

The glass samples were pulverized to the powder for solid-state $^{31}$P magic angle
spinning nuclear magnetic resonance (MAS-NMR) spectra. $^{31}$P MAS-NMR spectra were
measured to determine the phosphate structures in the glasses at 161.906 MHz in a 8 mm
rotor that was spinning at 5 kHz (Varian UNITY Inova 400 plus). A single pulse
experiment with $5 \mu$s pulse width, 60 s recycle delay, and a cumulative number of 64, was
performed for each sample. The chemical shift was referenced to the signal of NH$_4$H$_2$PO$_4$
as 1.0 ppm. The theoretical network connectivity ($NC_{\text{theor}}$), which is defined as the number of bridging oxygens per network forming element [12], was calculated using the following equation,

$$NC_{\text{theor}} = \frac{3[P_2O_5] - [CaO] - (2[TiO_2] \text{ or } 3[Nb_2O_5])}{[P_2O_5]}$$

(1)

where $[P_2O_5]$, $[CaO]$, $[TiO_2]$, and $[Nb_2O_5]$ are the molar fractions of phosphate, calcium oxide, titanium dioxide, and niobium pentoxide, respectively. The experimental network connectivity ($NC_{\text{exp}}$) was calculated based on the deconvolution of $^{31}$P MAS-NMR spectra, assuming the presence of $Q_{p}^0$ and $Q_{p}^1$ units.

The glasses density were measured by the Archimedes’ method using water as immersion fluid at room temperature: the glass fractures were prepared 100 ~ 300 mg and the water temperature was 25°C ($n = 3$). The oxygen density was calculated, to allow the calculation of the compactness of the glass network using the following equation [13,14]:

$$\rho_{\text{oxygen}} = \frac{M(O) \times ([CaO] + 5[P_2O_5] + 2[TiO_2] \text{ or } 5[Nb_2O_5])}{M(\text{glass}) / \rho_{\text{glass}}},$$

(2)

where $M(O)$ and $M(\text{glass})$ are the atomic weight of oxygen and the molar weight of the glass, respectively; $[CaO]$, $[P_2O_5]$, $[TiO_2]$, and $[Nb_2O_5]$ are the molar fractions of phosphate, calcium oxide, titanium dioxide, and niobium pentoxide, respectively; and $\rho_{\text{glass}}$ is the experimental density of the glass.
2.4 Characterization of dissolution in a Tris buffer solution

Glass samples were pulverized and sieved to provide particle sizes between 125 and 300 μm. A Tris buffer solution was prepared by dissolving 6.118 g of tris(hydroxymethyl)aminomethane (NH₂C(CH₂OH)₃, Kishida Chemical Co., Japan) in 1 L of distilled water at 37°C, and adjusting the pH to 7.4. Fifteen milligrams of the glass powders was soaked in 15 mL of the Tris buffer solution at 37°C for 7 days (n = 3). The concentrations of Ca²⁺, P⁵⁺, Ti⁴⁺, and Nb⁵⁺ ions in the solution were measured using ICP-AES.

3. Results

3.1 Glass formation

Optically clear glasses were obtained in the composition region with a Ca/P ratio of < 1.10 (nominal composition), while partially crystallized glasses were obtained with Ca/P ratios of ≥ 1.10. In the subsequent experiments, crystalline (opaque) parts were removed manually. ICP-AES analysis showed that the composition of the Ti-IGs was very close to the nominal composition, as shown in Table 1. The Nb-IGs, however, could not
be analyzed using ICP-AES, because the glass powders turned into a gel in acids such as 1N HCl and 1N HNO₃. The compositions of the Nb-IGs were therefore analyzed using EDX (Table 1); the amount of phosphorus was reasonably close to that shown in the nominal composition, and the amounts of calcium and niobium varied by approximately 2.5 mol%. Because the phosphorus Ka (2.013 eV) and niobium La (2.166 eV) peaks overlapped, it was difficult to accurately determine the composition. Hereafter, the glass codes (Ca/P ratio) estimated from the nominal compositions, are used in the discussion of the results.

3.2 Thermal properties

Figure 1 shows results for $T_g$, $T_c$, and the glassification degree for the glasses. $T_g$ and $T_c$ showed increasing trends with increases in the Ca/P ratio; the $T_g$ values varied in the region of 646°C to 684°C and 645°C to 684°C for the Ti-IGs and Nb-IGs, respectively, and the $T_c$ values varied in the region of 714°C to 735°C and 722°C to 737°C for the Ti-IGs and Nb-IGs, respectively. The glassification degree showed decreasing trends with increases in the Ca/P ratio; the values for the Ti-IGs varied between 0.05 and 0.08, and the values for the Nb-IGs varied between 0.06 and 0.09.
3.3 Glass structures

The phosphate groups in the glasses showed Raman bands corresponding to \(Q_p^0\) and \(Q_p^1\) groups, as shown in Fig. 2 (a, b), including the POP\(_{\text{sym}}\) stretching mode of the bridging oxygen in \(Q_p^1\) (750 cm\(^{-1}\)), the (PO\(_4\))\(_{\text{sym}}\) stretching mode of the non-bridging oxygen in \(Q_p^0\) (950 cm\(^{-1}\)), the (PO\(_3\))\(_{\text{sym}}\) stretching vibrations of the non-bridging oxygen in \(Q_p^1\) (1040 cm\(^{-1}\)) \[15\], and the P-O stretching of the \(Q_p^1\) chain terminator (1115 cm\(^{-1}\)) \[16\]. The Ti-IGs showed bands corresponding to the Ti-O stretching vibrations of TiO\(_6\) octahedrons (640 cm\(^{-1}\)), the Ti-O stretching vibrations of TiO\(_4\) tetrahedrons (875 cm\(^{-1}\)) \[17\], and P-O-Ti bonds (993 cm\(^{-1}\)) \[1,18,19\]. The Nb-IGs showed bands corresponding to the Nb-O vibrations of NbO\(_6\) octahedrons corner-linked in a three-dimensional network (640 cm\(^{-1}\)) \[20,21\], the Nb-O vibrations of NbO\(_4\) tetrahedrons (845 cm\(^{-1}\)) \[21\], the Nb-O bond vibrations in isolated NbO\(_6\) octahedral units (910 cm\(^{-1}\)) \[20,21\], and the Nb=O stretching vibration mode of the NbO\(_4\) terminal bond (990 cm\(^{-1}\)) \[22\]. The experimental Raman bands were simulated, assuming Gaussian lines. The integrated peak intensities of the deconvoluted bands were calculated; the integrated peak intensities of the phosphate, Ti-O, and Nb-O group bands were normalized by the sums \(I(\text{POP}_{\text{sym}}) + I((\text{PO}_4)_{\text{sym}}) + I(\text{P-O-Ti}) + I(\text{P-O stretch} \ Q_p^1) \text{ chain terminator}, \text{ and } I(\text{TiO}_6) + I(\text{TiO}_4) + I(\text{P-O-Ti}) \text{ and } I(\text{NbO}_{6, 3\text{D}}) + I(\text{NbO}_4) + I(\text{NbO}_{6, \text{isolated}}) + I(\text{Nb=O bond of}
NbO$_4$, terminal), respectively (Fig. 2 (c-f)), where $I$ denotes each peak amplitude. With increases in the Ca/P ratio in the Ti-IGs, the integrated peak intensities associated with the $Q_{p0}$ group and the P-O-Ti bonds increased, and those associated with the $Q_{p1}$ group decreased (Fig. 2 (c)). With increases in the Ca/P ratio in the Nb-IGs, the integrated peak intensities associated with the $Q_{p0}$ group increased, and those associated with the $Q_{p1}$ group decreased (Fig. 2 (d)). With increases in the Ca/P ratio in the Ti-IGs, the peak intensity associated with the TiO$_4$ tetrahedrons showed no significant changes, the peak intensity associated with the P-O-Ti bonds increased, and the peak intensity associated with the TiO$_6$ octahedrons decreased (Fig. 2 (e)); with increases in the Ca/P ratio in the Nb-IGs, the peak intensity associated with the NbO$_4$ tetrahedrons increased, and the peak intensity associated with the NbO$_6$ octahedrons decreased (Fig. 2 (f)).

$^{31}$P MAS-NMR spectra of the glasses are shown in Fig. 3 (a, b). The center peaks between 10 and −25 ppm were assigned to $Q_{p0}$ and $Q_{p1}$ units, and the remaining peaks observed on both sides of the center peaks were associated with spinning side bands. The experimental spectra were simulated, assuming Gaussian lines for the $Q_{p0}$ and $Q_{p1}$ units. With increases in the Ca/P ratio, the fractured peak top positions of $Q_{p0}$ low-field shifted from 0.8 to 2.0 ppm and from 0.6 to 2.2 ppm for the Ti-IGs and the Nb-IGs, respectively, and the fractured peak top positions of $Q_{p1}$ low-shifted from −6.9 to −2.7 ppm and from
−7.0 to −2.1 ppm for the Ti-IGs and the Nb-IGs, respectively, as shown in Fig. 3 (c, d). The peak integrated portions associated with the $Q_p^0$ and $Q_p^1$ groups in the glasses increased and decreased linearly, respectively, with increases in the Ca/P ratio. With increases in the Ca/P ratio, the $Q_p^0$ contents in the Ti-IGs and Nb-IGs increased from 33% to 66% and from 33% to 67%, respectively, and the $Q_p^1$ contents in the Ti-IGs and Nb-IGs decreased from 67% to 34% and from 67% to 33%, respectively, as shown in Fig. 3 (e, f).

Figure 4 shows the experimental and theoretical network connectivities of the glasses. With increases in the Ca/P ratio, $NC_{theor}$ for the Ti-IGs and the Nb-IGs decreased from 0.33 to -0.23 and from 0.51 to -0.21, respectively, and $NC_{exp}$ for the Ti-IGs and the Nb-IGs decreased from 0.67 to 0.34 and from 0.67 to 0.33, respectively.

3.4 Density of the glasses

The density of the Ti-IGs and the Nb-IGs increased from 3.00 to 3.05 g·cm$^{-3}$ and from 3.08 to 3.15 g·cm$^{-3}$, respectively, with increases in the Ca/P ratio, as shown in Fig. 5 (a). No significant difference in the oxygen density of the glasses was observed, only a slight decrease; the oxygen density in the Ti-IGs varied between 1.29 and 1.32 g·cm$^{-3}$, and that in the Nb-IGs varied between 1.18 and 1.21 g·cm$^{-3}$. 
3.5 Dissolution behaviors of the glasses

Figure 6 shows ion-release percentages from the glasses into the Tris buffer solution, relative to the original amount in the glasses. The solubility of the glasses was very low; less than 5% and 7% of all of the components were released from the Ti-IGs and the Nb-IGs, respectively, even after 7 days. With increases in the Ca/P ratio, the ion-release percentage for the Ti-IGs and Nb-IGs decreased from 5.0% to 3.5% and from 7.0% to 5.0%, respectively.

4. Discussion

4.1 Glassification degree

$T_g$ and $T_c$ increased for the Ti-IGs and the Nb-IGs—and their glassification degree decreased—with increases in the Ca/P ratio. The glasses showed low glassification degrees; a value of 0.05 was determined for the Ti-IGs ($Ca/P = 1.24$), and a value of 0.06 was determined for the Nb-IGs ($Ca/P = 1.30$). The glassification degree is an indication of the glass-forming ability; Ouchetto et al. reported a glassification degree of approximately 0.25 for a zinc metaphosphate glass, and a low value of approximately...
0.07 for an invert glass [11]. The results obtained here showed that the Ti-IGs and Nb-IGs had a tendency to induce crystallization during quenching, owing to insufficient amounts of a glass network former (i.e., phosphate).

With increases in the Ca/P ratio, the integrated peak intensity associated with the $Q^0_p$ group increased, and that associated with the $Q^1_p$ group decreased. The peak integrated portions for the phosphate groups (determined from the $^{31}$P MAS-NMR spectra for the Ti-IGs and Nb-IGs) showed that the $Q^0_p$ content increased to 66% and 67%, and the $Q^1_p$ content decreased to 34% and 33%, respectively, with increases in the Ca/P ratio. The laser Raman and $^{31}$P MAS-NMR spectra indicated a similar tendency; that is, increases in the $Q^0_p$ group content and decreases in the $Q^1_p$ group content. The Ca/P ratio of the glasses with $Q^0_p/Q^1_p = 1$ in the integrated peak portion for Ti-IGs or Nb-IGs was 1.10 or 1.14, respectively. As shown in Fig. 1, the glasses containing larger amounts of $Q^0_p$ group than $Q^1_p$ group (i.e., Ti-IGs with Ca/P $\geq 1.10$, and Nb-IGs with Ca/P $\geq 1.14$) showed a glassification degree of 0.05 $\sim$ 0.07; nearly clear glasses with partially crystallized portions were obtained.

4.2 Glass structure

The glass density increased with increases in the Ca/P ratio, despite the decrease
in $M_{(glass)}$, and the oxygen density of the glasses showed very little change (or decreased slightly). These results indicated that the glass networks became more densely packed with increases in the Ca/P ratio. Intermediate oxides—i.e., TiO$_2$, and Nb$_2$O$_5$—would have assisted in the formation of the glass network structure, even in the glasses containing numerous $Q^0_p$ group, although predictably their glass network would change to be less densely packed.

The $NC_{theor}$ values calculated using equation (1) were less than 0 with Ca/P ratios of $>1.13$ and $>1.21$ for the Ti-IGs and Nb-IGs, respectively; this meant that, theoretically, no glass network structure could form in these composition regions. That is, the intermediate oxides helped to form the glass network structure. The $NC_{exp}$ values were 0.34 and 0.33 for the Ti-IGs and Nb-IGs, respectively. Polyhedral TiO$_n$ or NbO$_n$ would have cross-linked the phosphate groups. Our previous work showed that Ti-IGs contain P-O-Ti bonds, and that the peak intensity in the Raman spectra increased with increases in the TiO$_2$ content [1]. Brow et al. and Segawa et al. reported P-O-Ti bonds in binary TiO$_2$-P$_2$O$_5$ glasses [18] and TiO$_2$-ZnO-P$_2$O$_5$ glasses [19]. Jazouli et al. and Mazali et al. reported P-O-Nb bonds in Na$_2$O-P$_2$O$_5$ glasses modified with a small amount of Nb$_2$O$_5$ [23], and in niobophosphate glasses containing predominantly $Q^0_p$ and $Qp'$ groups [24]. In the present glass system, the integrated peak intensity associated with the P-O-Ti bonds
increased with increases in the Ca/P ratio in the Ti-IGs; it is possible that the formation of P-O-Nb bonds increased with increases in the Ca/P ratio in the Nb-IGs.

\[ T_g \] values of the glasses were increased with increasing the Ca/P ratio, \( i.e., NC_{theor} \) and \( NC_{exp} \) were decreased. A similar trend has been observed for the glasses in the \( \text{P}_2\text{O}_5-\text{MgO} \) [25] and the \( \text{P}_2\text{O}_5-\text{CaO-Na}_2\text{O} \) [26] system. Mandlule \textit{et al.} reported, this trend can be explained by an increasing ionic contribution in the glass structure [26]. Glasses with low phosphate content, \( i.e., \) invert glasses, formed their network by interactions between short phosphate units and modifier ions [26]. Brow reported, invert glasses do not have a continuous random network and their structure consist of short phosphate unit and modifier ions linked through non-bridging oxygens [27]. The structures of the invert glasses were more influenced by P-O' Me\(^+\) (Me\(^+\) being a modifier oxide) inter-chain cross-links than P-O-P bond [26,27]. \( Q_p^0 \) group in the glasses were increased with increasing the Ca/P ratio, \( i.e., \) number of non-bridging oxygen in the glasses were increased. The increasing number of non-bridging oxygen in the glasses caused the increase in their \( T_g \), due to increase ionic contribution.

As shown in Fig. 3, the fractured peak top position associated with the phosphate groups showed a low-field shift with increases in the Ca/P ratio, which indicated a decrease in the electron density. Electrons belonging to the \( Q_p^0 \) and \( Q_p^1 \) groups were
pulled to the titanium or niobium side; the electron densities of the $Q_{p}^0$ and $Q_{p}^1$ groups therefore decreased with increases in the Ca/P ratio. Because the amount of P-O-Ti or P-O-Nb bonds in the glasses increased, the $Q_{p}^0$ and $Q_{p}^1$ groups had more chance to be influenced by the titanium or niobium, which have larger field strengths compared with calcium (Nb : 1.73, Ti : 1.04, Ca : 0.33 valence/Å$^2$) [28].

The integrated intensities associated with TiO$_4$ showed no significant difference when the Ca/P ratio in the Ti-IGs was increased; in contrast, the intensity associated with P-O-Ti increased, and that associated with TiO$_6$ decreased. The linking of the TiO$_4$ to the phosphate groups might have increased as a result of the decreases in the intensity associated with TiO$_6$. Brow et al. and Segawa et al. reported that titania linking to phosphate groups takes TiO$_6$ octahedron structure [18,19] in the CaO-TiO$_2$-P$_2$O$_5$ and TiO$_2$-ZnO-P$_2$O$_5$ glasses, respectively, consisting of $Q_{p}^2$ and $Q_{p}^1$ groups. Li et al. reported that, in P$_2$O$_5$-CaO-Na$_2$O-TiO$_2$ pyrophosphate glasses, titania enters the glass network as TiO$_4$ tetrahedrons connected to phosphate groups through P-O-Ti bonds [29]. Nagarjuna et al. reported that Ti$^{4+}$ ions enter the glass network as TiO$_4$ units and form the linkage of P-O-Ti bonds [30]. In the Nb-IGs, the integrated intensity associated with NbO$_6$ decreased with increases in the Ca/P ratio, and that associated with NbO$_4$ increased. Niobate linking to P-O-Nb bond takes NbO$_6$ octahedron structure, when the glasses were composed of
$Q_p^2$ and $Q_p^1$ groups [23,24,31]. Chu et al. and Hsu et al. reported that P-O-Nb bonds formed, and the partial NbO$_6$ octahedron structure gradually turned into a NbO$_4$ tetrahedron structure, with decreases in the content of P$_2$O$_5$ in the glasses [21,32]. The present glasses consisted of $Q_p^0$ and $Q_p^1$ groups; with Ca/P ratios $\geq 1.10$ in the Ti-IGs and $\geq 1.14$ in the Nb-IGs, they consisted predominantly of $Q_p^0$ groups. In the glasses with a Ca/P ratio of ~1.00, which consisted predominantly of $Q_p^1$ groups, TiO$_6$ or NbO$_6$ octahedrons cross-linked the phosphate groups to form P-O-Ti/Nb bonds. In $Q_p^0$-predominant compositions, i.e., in Ti-IGs with Ca/P $\geq 1.10$ and Nb-IGs with Ca/P $\geq 1.14$, the intermediate oxides took the form of tetrahedrons and cross-linked the phosphate groups.

4.3 Dissolution behaviors of the glasses

The glasses showed good chemical durability (up to 5% or 7% dissolution from the Ti-IGs or Nb-IGs after 1 week, respectively). Brauer et al. and Kishioka et al. reported that the chemical durability of P$_2$O$_5$-CaO-MgO-Na$_2$O-TiO$_2$ and Na$_2$O/K$_2$O-TiO$_2$-P$_2$O$_5$ glasses was improved by increases in the TiO$_2$ content, because the formed P-O-Ti bonds impeded the hydration of the phosphate groups [12,33]. Mazali et al. reported that the chemical durability of Li$_2$O-Nb$_2$O$_5$-CaO-P$_2$O$_5$ glasses was improved by the formation of
P-O-Nb bonds [24]. Masai et al. reported that the chemical durability of SrO-BaO-Nb_2O_5-
P_2O_5 glasses was improved by increasing the $Q_p^0$ content in the glasses, as a result of
delocalization of the P=O groups [34]. The chemical durability of the glasses was
improved when the Ca/P ratio was increased, because the number of P-O-Ti/Nb bonds
and delocalized P=O bonds increased with increases in the $Q_p^0$ content in the glasses. All
of the components in the glasses dissolved at similar rates; the glasses showed congruent
dissolution, which indicated that no selective ion leaching occurred. It is expected that it
will be facile to control the ion dissolution behavior of the present glasses, because of
their excellent chemical durability.

5. Conclusion

The structures and dissolution behaviors of glasses containing TiO_2 or Nb_2O_5
and large amounts of CaO were investigated. Glasses with a Ca/P ratio of ≥ 1.00 were
successfully prepared using a conventional melt-quenching method. In the glasses with
compositions of Ca/P > 1.10 in the Ti-IGs and Ca/P > 1.14 in the Nb-IGs, the amount of
$Q_p^0$ group was larger than the amount of $Q_p^+$ group. In the glasses with high $Q_p^0$ contents,
the intermediate oxides (TiO_2, Nb_2O_5) took the form of tetrahedrons (a shape similar to
that of the $Q_p^0$ group), and cross-linked the phosphate groups. The chemical durability of
the glasses increased with increases in the Ca/P ratio, because the number of P-O-Ti/Nb
bonds and $Q_p^0$ groups, which delocalized the P=O bonds, increased. The present glass
system shows potential as a candidate for the preparation of thin films on metal surfaces
via RF-sputtering, because of its excellent chemical durability.

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**Figure and table captions**

Figure 1: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), and glassification degree (($T_c - T_g)/T_g$) for (a) Ti-IGs, and (b) Nb-IGs.

Figure 2: Laser Raman spectra for (a) Ti-IGs, and (b) Nb-IGs, and normalized integrated peak intensities corresponding to phosphate groups of (c) Ti-IGs, and (d) Nb-IGs, (e) Ti-O groups of Ti-IGs, and (f) Nb-O groups of Nb-IGs, as a function of the Ca/P ratio in the glass.

Figure 3: $^{31}$P MAS-NMR spectra for (a) Ti-IGs, and (b) Nb-IGs, fractured peak top positions for (c) Ti-IGs, and (d) Nb-IGs, and peak integrated portions of phosphate groups for (e) Ti-IGs, and (f) Nb-IGs, as a function of the Ca/P ratio in the glass.

Figure 4: Experimental and theoretical network connectivities of (a) Ti-IGs, and (b) Nb-IGs, as a function of the Ca/P ratio in the glass.

Figure 5: (a) Densities of Ti-IGs and Nb-IGs, and (b) calculated oxygen densities of Ti-IGs and Nb-IGs, as a function of the Ca/P ratio in the glass.

Figure 6: Percentage of ions released into the Tris buffer solution, relative to the total amount in (a–c) Ti-IGs, and (d–f) Nb-IGs, for (a, d) Ca$^{2+}$, (b, e) P$^{5+}$, (c) Ti$^{4+}$, and (f) Nb$^{5+}$ ions, as a function of the Ca/P ratio in the glass.
Table 1: Nominal and analyzed glass compositions, and nominal Ca/P ratios of the glasses (glass code). The analyzed compositions are shown in round brackets with standard deviation.
Figures

Fig. 1

(a) 

(b)
Fig. 2
(a) Raman shift / cm\(^{-1}\) vs. Intensity (a.u.)
(b) Raman shift / cm\(^{-1}\) vs. Intensity (a.u.)
(c) Normalized integrated intensity of phosphate group vs. Ca/P ratio
(d) Normalized integrated intensity of phosphate group vs. Ca/P ratio
(e) Normalized integrated intensity of Ti-O group vs. Ca/P ratio
(f) Normalized integrated intensity of Nb-O group vs. Ca/P ratio
Fig. 3
Fig. 4
Fig. 5

(a) Density / g cm$^{-3}$

(b) Oxygen density / g cm$^{-3}$
Fig. 6
### Table 1

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<th>Ca/P ratio (Glass code)</th>
<th>Composition / mol%</th>
<th>Composition / atom%</th>
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Analyzed compositions of Ti-IGs and Nb-IGs were obtained by ICP-AES and EDS, respectively.