Stabilization of amorphous titanium pyrophosphate by niobium or tantalum doping

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Amorphous phosphates are very important for potential applications in optical communications and laser technologies [1, 2], and recently, in ultraviolet (UV)-ray shielding from sunshine [3]. In our previous paper, we have developed a series of amorphous cerium–titanium pyrophosphates ($Ce_{1-x}Ti_xP_2O_7$; $x = 0$–1) for UV-shielding materials [3]. These phosphates take full advantage of the amorphous state to attain effective UV shielding, and thus the feature characteristics deteriorate when the amorphous phosphates crystallize. Therefore, it is significantly important to stabilize the amorphous state in order to maintain the UV-ray shielding effect steadily. In the series of amorphous $Ce_{1-x}Ti_xP_2O_7$ phosphates, CeP_2O_7 and $Ce_{0.5}Ti_{0.5}P_2O_7$ can maintain the amorphous state up to 773 and 923 K, respectively [4–6]. However, TiP_2O_7 crystallizes even at 673 K, which is the lowest crystallization temperature among the $Ce_{1-x}Ti_xP_2O_7$ phosphates [6]. It is necessary to develop amorphous titanium phosphate, thermally stabilized above 673 K in order to apply the material to heat-stable paints, plastics and films or UV protection suits for welders. In this study, therefore, we aim to enhance the thermal stability of the amorphous TiP_2O_7 by doping niobium and tantalum as stabilizers, because the Nb and Ta ions have the same positive charge (5+) to phosphorous and can form amorphous phosphate easily [7].

Amorphous TiP_2O_7 was prepared by the co-precipitation method [3–5], and stabilization of the amorphous state was achieved by substituting phosphorus ion to niobium or tantalum ion in the amorphous phosphates in the ratio of 10–40 mol%. A titanium(IV) sulfate solution (30%) was dissolved in deionized water, adjusting the titanium concentration to be 0.1 mol dm^{-3}. An ethanol solution containing niobium chloride or tantalum chloride solution in a concentration of 0.05 mol dm^{-3} was also prepared. The titanium(IV) sulfate solution and a 0.1 mol dm^{-3} of sodium pyrophosphate aqueous solution were simultaneously dropped into the ethanol solution in the stoichiometric ratio. The resulting precipitates were separated by centrifuging, successively washed with deionized water for five times, and dried in an oven at 353 K for 24 hr. In order to evaluate the thermal stability of the amorphous phase, samples were calcined at 473–973 K for 5 hr at a heating rate of 100 K min^{-1}.

The compositions of the samples were confirmed by an X-ray fluorescent spectrometer (Rigaku ZEX-100e). The X-ray powder diffraction data were obtained by an X-ray diffractmeter (Rigaku Multiflex) with Cu-Kα radiation. Differential thermal analyses (DTA) of the amorphous samples were carried out at a heating rate of 10 K min^{-1} (Shimadzu DTG-60H) to determine their crystallization temperatures. Amorphous samples were also characterized by Raman spectroscopy (Kaiser Optical Systems, HoloProbe).

As a representative result, X-ray powder diffraction patterns of TiP_2O_7 and $Ti(P_{0.9}Nb_{0.1})_2O_7$ are shown in Fig. 1 for as-prepared and calcined samples at various temperatures. In both cases, the as-prepared samples were amorphous. In case of TiP_2O_7 without Nb, the amorphous phase is maintained up to 623 K and crystalline TiP_6O_{23} phase appears after heating above 623 K. The amorphous state of the Nb-doped sample was maintained up to 923 K, which is 300 K higher than that of the sample without Nb. After calcination above 923 K, formation of crystalline phases of $TiNb(PO_4)_3$ and Nb_2O_3 were observed. Therefore, the stabilizing effect of this amorphous phase is apparently identified by Nb doping.

Fig. 2 depicts the composition dependence of crystallization temperature of the $Ti(P_{1-x}M_x)_2O_7$ (M = Nb or Ta; $x = 0, 0.1, 0.2, 0.3,$ and 0.4) determined by their DTA measurements. Comparing the sample containing Nb with that of Ta, the stabilization of amorphous phase by the Ta doping is more effective than that by Nb, particularly at higher content region of the dopants.

In order to identify the reason for the stabilization of the amorphous state in TiP_2O_7, the changes in the bonding state of the amorphous substance were discussed using Raman spectra as illustrated in Fig. 3. By the doping of Nb or Ta ion in the amorphous TiP_2O_7, the relative Raman intensity at 337 and 762 cm^{-1} corresponding to the O—P—O bending and the P—O—P symmetric stretching modes decreased, while the Nb—O or Ta—O stretching mode at around 645 cm^{-1} increased [7–10]. In case of $Ti(P_{1-x}Nb_x)_2O_7$, a new peak appeared at about 276 cm^{-1} by the Nb doping. This peak is associated with vibration modes involving $P_2O_7^{4-}$ and isolated PO_4^{3-} groups present in the samples [10]. A similar peak was also observed in the $Ti(P_{1-x}Ta_x)_2O_7$ samples.

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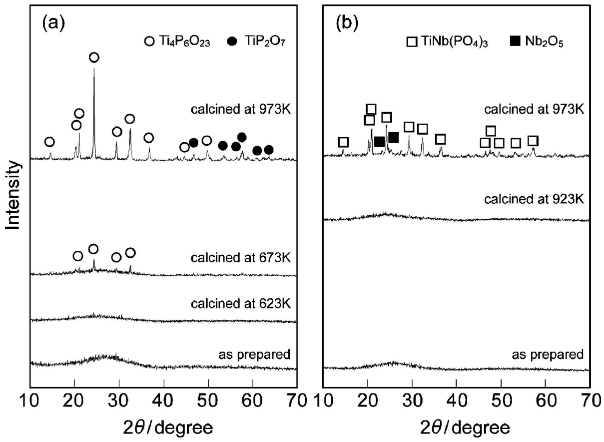

Figure 1 X-ray powder diffraction patterns of (a) TiP_2O_7 and (b) $Ti(P_{0.9}Nb_{0.1})_2O_7$ samples as prepared and calcined at various temperatures.

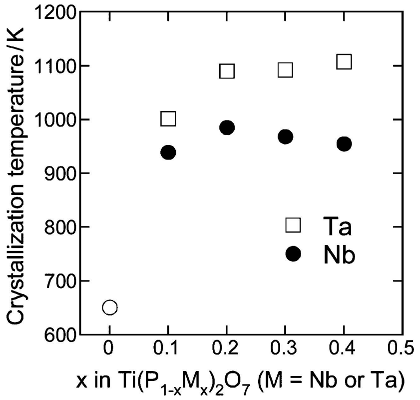

Figure 2 Compositional dependence of crystallization temperatures of $Ti(P_{1-x}M_x)_2O_7$ (M = Nb or Ta; x = 0, 0.1, 0.2, 0.3, and 0.4).

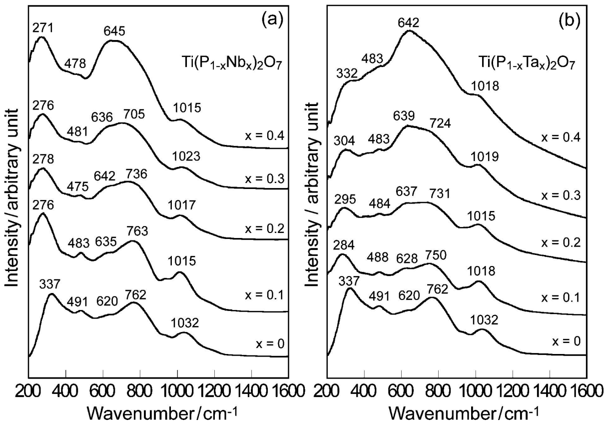

Figure 3 Raman spectra of the amorphous (a) $Ti(P_{1-x}Nb_x)_2O_7$ and (b) $Ti(P_{1-x}Ta_x)_2O_7$ (x = 0, 0.1, 0.2, 0.3, and 0.4).

The more is the doping of Nb or Ta in amorphous TiP_2O_7, the higher is the Raman intensity at around 645 cm^{-1}. The peak at 645 cm^{-1} is vibration mode assigned to MO_6 or MO_4 (M = Nb or Ta) groups, and increase in the intensity of this band corresponds to the promotion of non-bridging oxygen species in the samples. Because the presence of the bridging oxygen facilitates crystallization in phosphate grasses [11], it is concluded that the stabilization of the amorphous state is attributable to the breaking of bridging oxygen in the P—O—P bond in the pyrophosphate structure and simultaneous formation of the non-bridging oxygen in the M—O bond in MO_6 or MO_4 (M = Nb or Ta) groups [10].

Comparing the main peaks observed in the $Ti(P_{1-x}Ta_x)_2O_7$ samples with those in the $Ti(P_{1-x}Nb_x)_2O_7$ samples, the M—O bond (M = Ta) at around 640 cm^{-1} becomes the highest at $x = 0.3$ and 0.4 of $Ti(P_{1-x}Ta_x)_2O_7$, which indicates that the amount of the non-bridging oxygen produced in $Ti(P_{1-x}Ta_x)_2O_7$ is higher than that in $Ti(P_{1-x}Nb_x)_2O_7$, especially in the samples of high M (M = Nb or Ta) content of $x \geq 0.3$. This would be the reason for the $Ti(P_{1-x}Ta_x)_2O_7$ samples of $x = 0.3$ and 0.4 to maintain amorphous state with more stability than the $Ti(P_{1-x}Nb_x)_2O_7$ samples as described in Fig. 2. The thermal stability of the amorphous state in these samples can satisfy the demand in the applications for UV-shielding plastics and films, which are sometimes heated (maximum 673 K) in their production process.

In summary, it becomes possible to stabilize amorphous TiP_2O_7 by acting on the bonding state of oxygen in the phosphate anion, i.e. by partially substituting phosphorous site with niobium or tantalum ion in the amorphous phosphate. Raman spectra analysis elucidates that this stabilizing effect is induced by the formation of non-bridging oxygen in the Nb—O or Ta—O bond, which effectively suppresses crystallization of the amorphous phosphate. Such results suggest that suitably engineered amorphous phosphates based on TiP_2O_7 may be promising candidates as effective materials for UV-ray shielding agents not only in cosmetics and paints but also in plastics and films.

Acknowledgments

The authors sincerely thank Dr. Kuniaki Murase and Prof. Dr. Yasuhiro Awakura (Kyoto University) for their assistance with the Raman spectra measurements. This work was supported by the Industrial Technology Research Grant Program in 02 (Project No. 02A27004c) and the Nanotechnology Materials Program—Nanotechnology Particle Project from the New Energy and Industrial Technology Development Organization (NEDO) based on funds provided by the Ministry of Economy, Trade and Industry, Japan (METI).

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Received 24 August
and accepted 29 October 2004