doi:10.1246/cl.2012.555

Preparation of α-Zirconium Phosphate from Fluorozirconate and Phosphoric Acid by Liquid-phase Deposition

Seiichi Tahara,[1] Yoshie Takakura,[2] and Yoshiyuki Sugahara*[2,3]
[1] *Waseda Research Institute for Science and Engineering, Waseda University,*
3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555
[2] *Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University,*
3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555
[3] *Kagami Memorial Laboratory for Materials Science and Technology, Waseda University,*
2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051

(Received February 10, 2012; CL-120111; E-mail: ys6546@waseda.jp)

α-Zirconium phosphate (α-ZrP) was prepared by liquid-phase deposition. Boric acid was added to a solution containing $[ZrF_6]^{2-}$ anions, and phosphoric acid dropwise to cause slow decomposition of $[ZrF_6]^{2-}$ and the subsequent reaction with H_3PO_4 to form α-ZrP. X-ray diffraction, scanning electron microscopy, solid-state ^{31}P nuclear magnetic resonance spectroscopy, infrared spectroscopy, thermogravimetry, and elemental analyses indicate the formation of single-phase α-ZrP.

Layered metal phosphates, in particular zirconium phosphates, have been attracting considerable attention because of their potential catalytic and ion-exchange applications.[1,2] The α-type of zirconium phosphate (α-$Zr(O_3POH)_2\cdot H_2O$; α-ZrP) consists of nanosheets of tetravalent zirconium cations and hydrogenphosphate anions (HPO_4^{2-}). Three oxygen atoms per hydrogenphosphate group are bound to zirconium cations to form the nanosheets, and the remaining oxygen is present as an OH group, which is oriented toward the interlayer region.[3] Since OH groups on the interlayer surface can interact with basic compounds, such as organic amines to form intercalation compounds, a variety of intercalation compounds of α-ZrP have been prepared.[1,2]

The preparation of single-phase α-ZrP generally requires complicated procedures, since an amorphous gel can be easily formed. Two approaches have been commonly used for the preparation of single-phase α-ZrP.[1] One approach to formation of single-phase α-ZrP is refluxing of an amorphous gel in an aqueous H_3PO_4 solution.[4] A long refluxing time (typically 300 h) is required, however, for the conversion of the amorphous gel to crystalline α-ZrP. In the other approach, crystalline α-ZrP is obtained by precipitation from hydrofluoric acid dissolving zirconium salt and phosphoric acid.[5,6] Since fluoride anions are known to form fluorozirconate complexes with zirconium cations, the reaction can be controlled by the concentration of hydrofluoric acid. When the concentration of hydrofluoric acid is slowly decreased via volatilization, the fluorozirconate complexes are gradually dissociated and α-ZrP precipitation begins. The decrease rate of the hydrofluoric acid concentration is very important; a rapid decrease causes the formation of an amorphous gel. Single-phase α-ZrP can also be obtained by hydrothermal synthesis[7] or sol–gel process.[8] Its high-yield preparation was recently achieved by addition of an aqueous H_3PO_4 solution to solution of a Zr^{4+} salt and oxalic acid.[9]

The liquid-phase deposition (LPD) process has been developed for direct deposition of metal oxides or hydroxides from anionic metal–fluoro complexes.[10,11] The process for oxides can be expressed by the following equilibrium:

$$MF_x^{(x-2n)-} + nH_2O + (x-2n)H^+ \rightleftharpoons MO_n + xHF \qquad (1)$$

It should be noted that oxide anions are provided by water. The deposition of target metal oxides and metal hydroxides is dramatically enhanced by the addition of boric acid, since the fluoride anions are captured from the metal–fluoro complexes by forming BF_4^- anions. Thus, if phosphoric acid can be utilized as a source of hydrogenphosphate or dihydrogenphosphate anions, the formation of metal phosphate can be expected. In terms of zirconium compounds, the LPD process has been utilized for the preparation of ZrO_2.[12,13]

Here we report the first preparation of α-ZrP by the LPD process. The product was characterized by X-ray diffraction (XRD; Rigaku RINT-2500, monochromated Cu Kα radiation), scanning electron microscopy (SEM; Hitachi S-2500CX), infrared (IR) absorption spectroscopy (JASCO FT/IR-460 Plus) using KBr disc, solid-state ^{31}P nuclear magnetic resonance (NMR; JEOL CMX-400) spectroscopy employing magic angle spinning (MAS) (161.84 MHz, spinning rate: 8 kHz), and thermogravimetry (TG; Rigaku TG-8120 Thermo plus EVO) in the range from room temperature to 900 °C with heating rate of 10 °C min^{-1} under N_2 flow. The amounts of zirconium and phosphorous were determined by inductively coupled plasma emission spectrometry (ICP; Thermo Jarrell Ash, ICAP-574II) after dissolution with a HNO_3–H_2SO_4–HF mixture. The detection of boron and fluorine was conducted by using wavelength-dispersive X-ray fluorescence spectroscopy (XRF; Rigaku, ZSX PrimusII).

For the preparation of α-ZrP, 5.17 g of $ZrOCl_2\cdot 8H_2O$ and 6 mL of H_3PO_4–water mixture (14.6 mol L^{-1}) were added to 30 mL of water, and the mixture was stirred at room temperature to form a white gel. Hydrofluoric acid (ca. 28 mol L^{-1}) was added until the white gel was completely dissolved, and 0.5 mol L^{-1} boric acid was then added dropwise to the solution to deposit a white precipitate. A white powdery product was obtained after centrifugation, followed by washing with water and drying at room temperature.

Figure 1 demonstrates the XRD pattern of the product deposited from the $ZrOCl_2\cdot 8H_2O$–H_3PO_4 solution. In the XRD pattern of the product, all the reflections are indexed as a monoclinic cell with $a = 0.9042(4)$, $b = 0.5287(2)$, $c = 1.5417(6)$ nm and $\beta = 101.63(4)°$, which coincides closely with the reported lattice parameters of α-ZrP, $a = 0.9060(2)$, $b = 0.5297(1)$, $c = 1.5414(3)$ nm and $\beta = 101.71(2)°$.[3] These XRD results indicate the formation of α-ZrP by the LPD process.

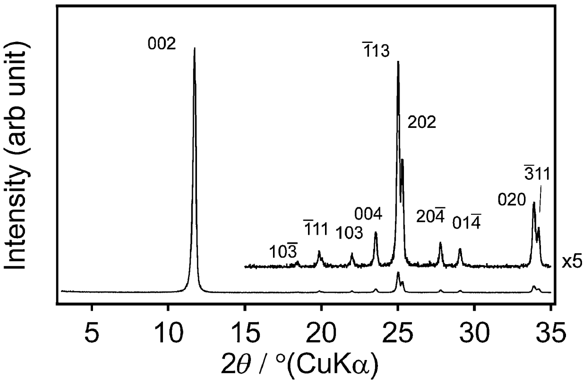

Figure 1. XRD pattern of product deposited from the $ZrOCl_2 \cdot 8H_2O$–H_3PO_4 solution.

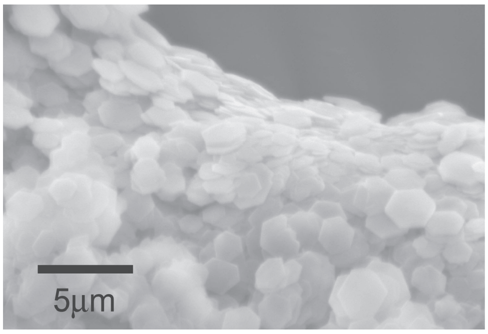

Figure 2. SEM image of product deposited from the $ZrOCl_2 \cdot 8H_2O$–H_3PO_4 solution.

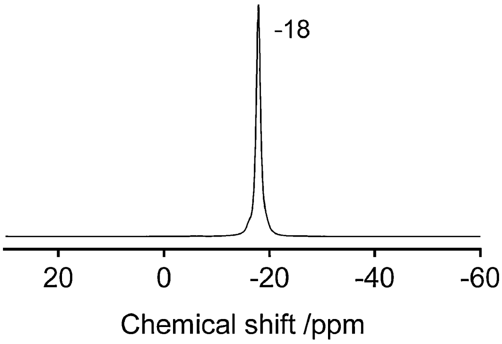

Figure 3. Solid-state ^{31}P MAS NMR spectrum of product deposited from the $ZrOCl_2 \cdot 8H_2O$–H_3PO_4 solution.

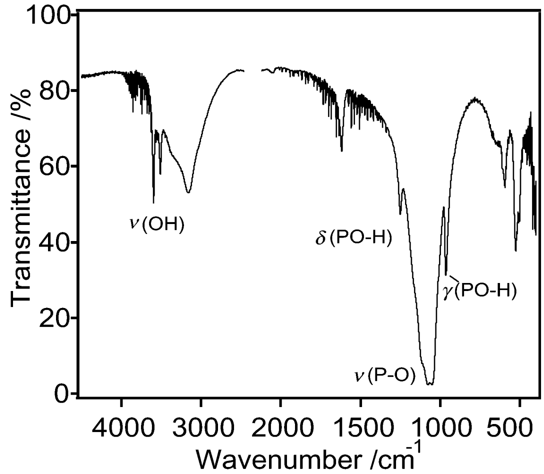

Figure 4. IR spectrum of product deposited from the $ZrOCl_2 \cdot 8H_2O$–H_3PO_4 solution.

A SEM image of the product is shown in Figure 2. In the SEM image, plate-like particles, typical morphology for layered compounds, are observed. The particle sizes of the products are in the range of 2–3 µm. A similar particle size range was observed when we prepared α-ZrP by the precipitation from hydrofluoric acid dissolving zirconium salt and phosphoric acid via volatilization of hydrofluoric acid as previously reported.[5,6] In addition, no other type of morphology is observed, suggesting the absence of any by-products.

The solid-state ^{31}P MAS NMR spectrum of the product is shown in Figure 3. In the spectrum, an intense signal is observed at -18 ppm and assigned to the $(Zr–O)_3P(OH)$ environment of α-ZrP.[14] It should be noted that no signals due to other phosphorus environments, which could be ascribed to amorphous phases, are present.

Figure 4 shows FT-IR spectrum of the product. In the spectrum, the bands observed at 3700–3000, 1250, 1100–1000, and 963 cm^{-1} are assignable to ν(OH), δ(PO–H), ν(P–O), and γ(PO–H) mode, respectivery.[15] Two additional sharp bands at around 3500 and 3600 cm^{-1} are due to O–H stretching modes of POH groups and water of crystallization, respectivly.[16]

The TG curve of the product is shown in Figure 5. It was reported that decomposition of α-ZrP occurred by the loss of water of crystallization from 70 to 400 °C and that the subsequent condensation reaction between POH groups led to the formation of ZrP_2O_7 from 400 to 900 °C.[9] In this study, 6.1% and 6.0% of mass loss are observed from 70 to 400 °C and from 400 to 900 °C, respectively, which is consistent with the ideal mass losses (6.0% for each). The mass gradually decreased from 70 to 400 °C, which was reported to be caused by the variation in crystal size; the temperature range for the loss of water of crystallization was shifted toward high temperature with increasing crystal size.[9]

The ICP result of the product showed that P/Zr was 2.0, which is well consistent with the ideal ratio for α-ZrP. In addition, no boron and fluorine were detected by XRF analysis. The XRD, SEM, solid-state ^{31}P MAS NMR, IR, and elemental analysis results thus clearly indicate the formation of α-ZrP, with no formation of amorphous ZrP gels.

In this study, H_3PO_4 is a source of hydrogenphosphate anions. It was revealed, on the other hand, that the zirconium cations in concentrated hydrofluoric acid formed the $[ZrF_6]^{2-}$ complex.[13,17] Since the solution is acidic throughout the reaction because of the presencse of acid (H_3PO_4 and HF), the overall reaction could be expressed as follows:

$$[ZrF_6]^{2-} + 2H_3PO_4 + 2H^+ \rightarrow Zr(O_3POH)_2 + 6HF \quad (2)$$

H_3BO_3 easily reacts with HF:

$$H_3BO_3 + 4HF \rightarrow BF_4^- + H_3O^+ + 2H_2O \quad (3)$$

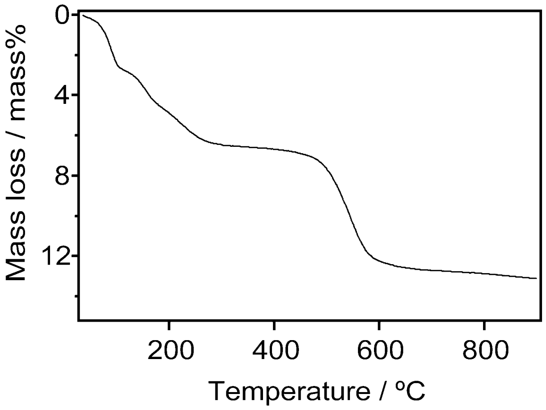

Figure 5. TG curve of product deposited from the $ZrOCl_2 \cdot 8H_2O$–H_3PO_4 solution.

The dropwise addition of H_3BO_3 thus leads to the slow decomposition of $[ZrF_6]^{2-}$ and the subsequent reaction with H_3PO_4 to form single-phase α-ZrP.

In summary, we have demonstrated a novel preparation of α-ZrP by the LPD process. This approach is highly attractive for the preparation of zirconium phosphate, because it is a very simple procedure and requires a very short reaction time. We believe the present approach appears to be applicable to the preparation of a variety of layered metal phosphates and metal organophosphonates.

This work was financially supported in part by Grant-in-Aid for challenging Exploratory Research (No. 20655047) and the Global COE for Practical Chemical Wisdom from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.* **1996**, *8*, 291.
2 C. V. Kumar, A. Bhambhani, N. Hnatiuk, in *Handbook of Layered Materials*, ed. by S. M. Auerbach, K. A. Carrado, P. K. Dutta, CRC Press, New York, **2004**, p. 313.
3 J. M. Troup, A. Clearfield, *Inorg. Chem.* **1977**, *16*, 3311.
4 A. Clearfield, J. A. Stynes, *J. Inorg. Nucl. Chem.* **1964**, *26*, 117.
5 G. Alberti, E. Torracca, *J. Inorg. Nucl. Chem.* **1968**, *30*, 317.
6 G. Alberti, U. Costantino, R. Giulietti, *J. Inorg. Nucl. Chem.* **1980**, *42*, 1062.
7 L. Sun, W. J. Boo, D. Sun, A. Clearfield, H.-J. Sue, *Chem. Mater.* **2007**, *19*, 1749.
8 H. Benhamza, P. Barboux, A. Bouhaouss, F.-A. Josien, J. Livage, *J. Mater. Chem.* **1991**, *1*, 681.
9 D. Capitani, M. Casciola, A. Donnadio, R. Vivani, *Inorg. Chem.* **2010**, *49*, 9409.
10 H. Nagayama, H. Honda, H. Kawahara, *J. Electrochem. Soc.* **1988**, *135*, 2013.
11 T. P. Niesen, M. R. De Guire, *J. Electroceram.* **2001**, *6*, 169.
12 K. Kuratani, M. Uemura, M. Mizuhata, A. Kajinami, S. Deki, *J. Am. Ceram. Soc.* **2005**, *88*, 2923.
13 T. Yao, T. Inui, A. Ariyoshi, *J. Am. Ceram. Soc.* **1996**, *79*, 3329.
14 N. J. Clayden, *J. Chem. Soc., Dalton Trans.* **1987**, 1877.
15 R. C. T. Slade, J. A. Knowles, D. J. Jones, J. Rozière, *Solid State Ionics* **1997**, *96*, 9.
16 M. E. Garcia, J. L. Naffin, N. Deng, T. E. Mallouk, *Chem. Mater.* **1995**, *7*, 1968.
17 V. P. Nesterenko, *J. Therm. Anal. Calorim.* **2005**, *80*, 575.