

Synthesis and electrical conductivity of bulk tetra-valent cerium pyrophosphate

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Tetra-valent cerium pyrophosphate was synthesized from cerium oxide and phosphoric acid by heating. The sintering processes, pressure-less sintering (PLS), spark plasma sintering (SPS), and hydrothermal hot pressing (HHP), were attempted to form bulk pyrophosphate. Furthermore, the electrical conductivity of bulk cerium pyrophosphate was investigated. Tetra-valent cerium pyrophosphate was synthesized by heating at 700 °C for 20 hours. The hydrothermal hot pressing process was a suitable method to synthesize bulk tetra-valent cerium pyrophosphate.

Key words: Cerium phosphate, Spark plasma sintering, Hydrothermal hot pressing, Electric conductivity.

Introduction

As a new clean energy, fuel cell technology has been studied in recent decades. Solid oxide fuel cells (SOFC) and polymer electrolyte fuel cells (PEFC) are well known and investigated to work at high and low temperatures, respectively. In a middle temperature, a phosphate material work as a solid state electrolyte [1-3].

Phosphates are transformed to other forms of phosphates by hydrolysis and dehydration reactions at elevated temperatures [4, 5]. Polyphosphate and ultraphosphate are included in a group of condensed phosphates. Polyphosphate has a chain structure in which the PO₄ unit shares two oxygen atoms and ultraphosphate has a network structure. These condensed phosphates have the possibility to have novel functional properties. Orthophosphate has been mainly investigated for many uses, on the other hand, condensed phosphates have been little studied.

In previous work, a condensed phosphate had a higher conductivity than an orthophosphate, because a part of condensed phosphate reacted with water in the atmosphere to produce protons [2, 3]. Because rare earth phosphates have high melting points, these are suitable materials as

solid state electrolytes for use at middle temperatures. In rare earth condensed phosphates, there are polyphosphates (R(PO₃)₃, R; rare earth cation) and ultraphosphates (RP₅O₁₄). In addition to these phosphates, tetra-valent cerium pyrophosphate (CeP₂O₇) and polyphosphate (Ce(PO₃)₄) are formed because the tetra-valent cerium cation is relatively stable. These materials are expected to have unique electric conductivities, compared with other rare earth phosphates. However, it is difficult to determine the conductivity of a target cerium phosphate, because a mixture of some types of cerium phosphates is formed.

The electric conductivity of a tri-valent rare earth phosphate is improved by the doping with a bi-valent cation, for example Sr²⁺ [3]. This is considered that the addition of a lower valent cation produces a cation defect. Therefore, a tri-valent rare earth cation was doped into tetra-valent cerium pyrophosphate to improve the electrical conductivity.

For an estimation of the electric conductivity, a bulk phosphate was required. It is difficult to synthesize a bulk phosphate without the decomposition of the phosphate structure. Tetra-valent cerium pyrophosphate transforms to cerium oxide losing P₂O₅ at high temperature in the following equation:



Therefore, the sintering process and conditions are very important to obtain high density bulk phosphates [6-10]. In this study, tetra-valent cerium phosphate was synthe-

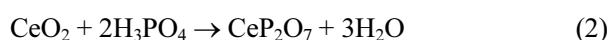
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Experimental

Preparation of cerium pyrophosphate

A mixture of cerium oxide and phosphoric acid in the molar ratio of $P/Ce = 2$ was kept at $100\text{ }^{\circ}\text{C}$ for 40 hours. Then the mixture was heated to the target temperature unhurriedly and held for 20 hours. Tetra-valent cerium pyrophosphate was formed in the following equation:



1 mol% of cerium was substituted by yttrium, gadolinium, and ytterbium. These mixtures were treated by the same heating process as the un-doped mixture.

For synthesis of bulk samples that had a high density, the pyrophosphates obtained were treated in a planetary-mill for 30 minutes. The planetary mill had five balls (15 mm diameter, ZrO_2) and a pot (40 mm inside diameter, 40 mm depth, ZrO_2). The weight ratio of sample/balls was 10/45.

Synthesis of bulk cerium pyrophosphates

For the synthesis of bulk cerium pyrophosphate without chemical decomposition, three processes were examined in this study. First, phosphate materials were pressed into a pellet and then heated at several temperatures for 20 hours. A spark plasma sintering (SPS) process was also tried to obtain high density bulk pyrophosphates. Phosphates were set in carbon mold, and then heated rapidly to a high temperature in a vacuum chamber. The average heating rate was about $80\text{ K}\cdot\text{minute}^{-1}$ and the sintering time was 5 minutes in this process. The phosphates were also used as the starting powder for a hydrothermal hot pressing (HHP) method. The mixture of phosphate powder (2 g) and water (0.1 ml) were set in a mold and mechanically pressed with a uni-axial pressure (40 MPa) and subsequently heated at $200\text{ }^{\circ}\text{C}$ for 2 hours.

Electrical conductivity of bulk tetra-valent cerium pyrophosphate

The electrical conduction properties of the un-doped and the trivalent rare earth doped CeP_2O_7 were investigated using conductivity measurements at $400\text{--}650\text{ }^{\circ}\text{C}$ under various conditions. Conductivity measurements in a D_2O -containing atmosphere were applied to identify protonic conduction.

Results and Discussion

Preparation of cerium pyrophosphate

It is difficult to react cerium oxide with phosphoric acid

at room temperature. Because the mixture of cerium oxide and phosphoric acid hardly reacted to cerium phosphates, samples scattered by heating. Therefore, the mixture was slowly heated to obtain tetra-valent cerium pyrophosphate. Suitable conditions were to heat at $700\text{ }^{\circ}\text{C}$ for 20 hours. Fig. 1 shows XRD patterns of samples prepared with and without the dopants. All samples showed the XRD peaks of tetra-valent cerium pyrophosphate. The peaks were not shifted and broadened by the addition of tri-valent rare earth cations.

To obtain high density bulk phosphate, phosphate powder was milled to smaller particles. Fig. 2 shows the particle size distribution of samples milled for 0 and 30 minutes. The particle size of cerium pyrophosphate became smaller with the mechanical treatment.

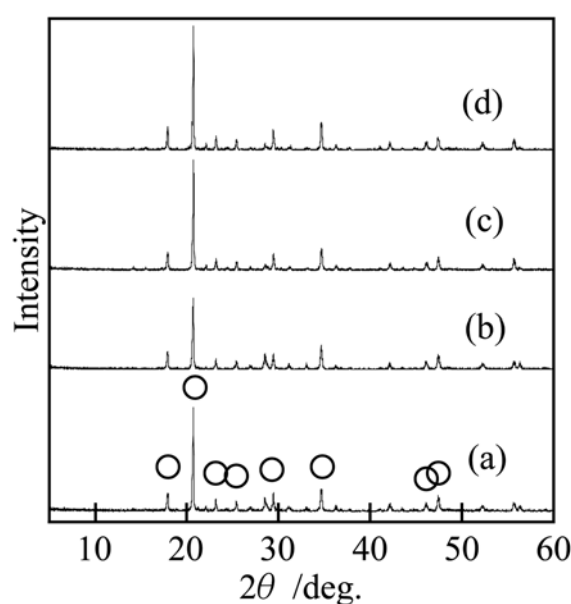


Fig. 1. XRD patterns of samples heated at $700\text{ }^{\circ}\text{C}$ for 20 hours, ○ ; CeP_2O_7 , (a) non doped, (b) Y doped, (c) Gd doped, and (d) Yb doped.

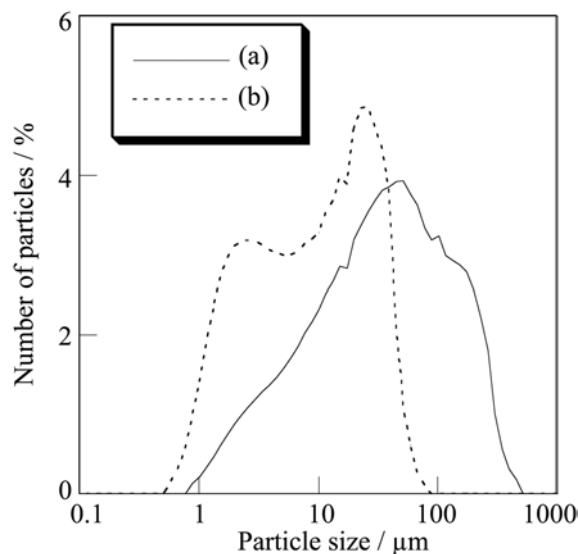
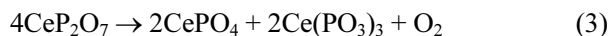


Fig. 2. Particle size distribution of CeP_2O_7 treated for (a) 0 and (b) 30 minutes with a planetary-mill.

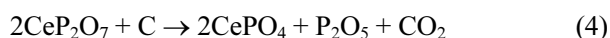
Synthesis of bulk cerium pyrophosphate

Table 1 shows the results on the pressure-less sintering process. By sintering at 800 °C for 20 hours, the bulk phosphate was too weak to measure the density. Tetra-valent cerium pyrophosphate decomposed to tri-valent cerium orthophosphate, CePO_4 , and polyphosphate, $\text{Ce}(\text{PO}_3)_3$ by calcinations at above 825 °C. The decomposition reaction was considered to take place in the following reaction:



This pressure-less sintering, as generally used, was not an appropriate method to synthesize the bulk phosphate.

Two points were considered to decompose cerium phosphate, one was to heat for a long time, and another one was at a high temperature. Because the spark plasma sintering (SPS) method is known to synthesize bulk samples in a short time, it was tried to obtain the bulk polyphosphate. Table 2 shows the results with CeP_2O_7 using the SPS method. The phosphate material was decomposed to a mixture of CePO_4 and $\text{Ce}(\text{PO}_3)_3$ by sintering at 900 °C for 5 minutes. By sintering at 870 °C, the phosphate did not decompose, however the peak intensity became weak in the XRD analysis. A certain part of pyrophosphate was considered to change to an amorphous phase, because the graphite mold and the vacuum produced a reducing atmosphere. A typical reaction is expressed in the following equation:



This sintering process was also considered as unsuitable for the measurement of electrical conductivity.

Another aspect in the decomposition of a target phosphate structure is to sinter at a high temperature in a pressure-less sintering process. To synthesize the bulk phosphate at a lower temperature, hydrothermal hot pressing (HHP) method was tried. In a previous study, the sintering conditions of tetra-valent cerium polyphosphates were studied in a hydrothermal hot pressing process [11]. Over 85% relative density was obtained in the synthesis of

bulk $\text{Ce}(\text{PO}_3)_4$. Therefore, we synthesized bulk cerium pyrophosphate using the same conditions as with cerium polyphosphate in a hydrothermal hot pressing process. This sintering process produced above 85% relative density of bulk CeP_2O_7 . These bulk samples were used for the measurement of electrical conductivity.

Electric conductivity of tetra-valent cerium pyrophosphate bulks

Fig. 3 shows the electric conductivity of Gd doped CeP_2O_7 in H_2O , D_2O and a dry atmosphere. This material indicated the same range of conductivity as with Gd doped $\text{Ce}(\text{PO}_3)_4$ [11]. Fig. 4 shows H/D isotope effect on the conductivity of Gd doped CeP_2O_7 . The Gd doped CeP_2O_7 indicated a value the near the square root of 2. Proton conductivity is considered to be predominant in these materials. This tendency was the same as that with rare earth doped cerium polyphosphates [11]. These tetra-

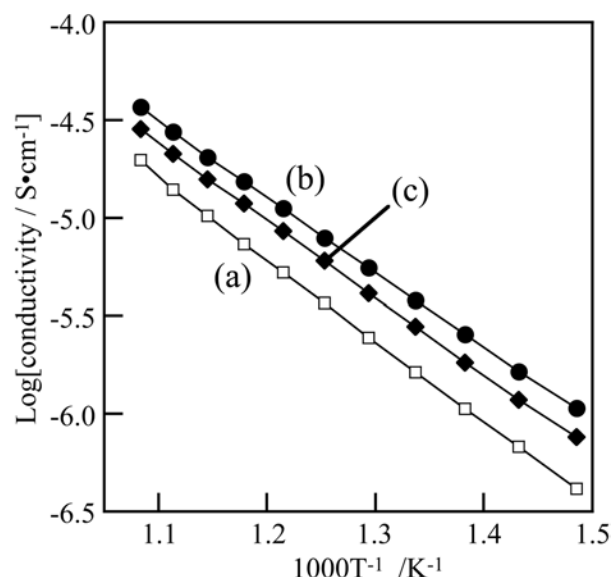


Fig. 3. Conductivity of Gd doped CeP_2O_7 in various conditions, (a) dry, (b) H_2O , and (c) D_2O (H_2O , D_2O 4.2 kPa).

Table 1. Experimental condition and results of cerium phosphates using the pressure-less sintering (PLS) process

Sample	Temperature/°C	Heating time/h	Composition after sintering	Density/ $\text{g}\cdot\text{cm}^{-3}$
CeP_2O_7	800	20	CeP_2O_7	X
CeP_2O_7	825	20	$\text{CeP}_2\text{O}_7 + \text{CePO}_4 + \text{Ce}(\text{PO}_3)_3$	-
CeP_2O_7	850	20	$\text{CePO}_4 + \text{Ce}(\text{PO}_3)_3$	-

X; difficult to measure because sample was too weak.

-; not calculated because chemical structure is not target cerium pyrophosphate.

Table 2. Experimental conditions and results of cerium pyrophosphates using the spark plasma sintering (SPS) process

Temperature/°C	Heating time/minute	Composition after sintering	XRD peak intensity after/before sintering	Density/ $\text{g}\cdot\text{cm}^{-3}$	Relativedensity/%
800	5	CeP_2O_7	6/50	2.57	78.5
870	0	CeP_2O_7	4/50	2.57	78.7
900	5	$\text{CeP}_2\text{O}_7 + \text{CePO}_4$	3/50	2.88	88.1
1050	5	$\text{CePO}_4 + \text{Ce}(\text{PO}_3)_3$	6/50	3.80	115.8

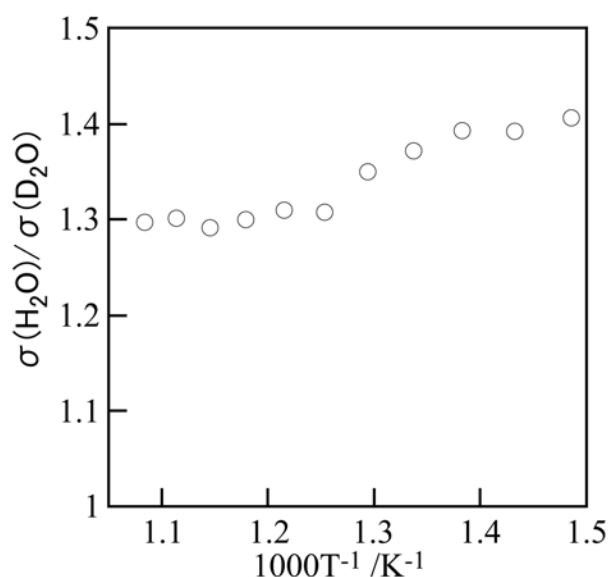


Fig. 4. H/D isotope effect on conductivity of Gd doped CeP_2O_7 .

valent cerium phosphates had a lower electrical conductivity than tri-valent cerium orthophosphate [12]. Cerium orthophosphate gave a higher electrical conductivity than other rare earth orthophosphates [12]. This was considered as coming from the existence of tetra-valent cerium phosphates, however this could not argue from the results obtained in this study. The oxidation/reduction reactions of cerium cation in phosphate materials were considered to be important, because only a mixture of tri- and tetra-valent rare earth phosphates would not give a high electrical conductivity.

Conclusions

Tetra-valent cerium pyrophosphate was synthesized from

cerium oxide and phosphoric acid by heating at 700 °C for 20 hours. The hydrothermal hot pressing process was shown to be a suitable method to synthesize bulk tetra-valent cerium pyrophosphate. This material gave the same range of conductivity with tetra-valent cerium polyphosphate in a previous study. Proton conductivity was considered to be predominant in these materials.

References

1. K. Amezawa, Y. Tomii and N. Yamamoto, *Solid State Ionics*, 176 (2005) 135-141.
2. K. Amezawa, Y. Tomii and N. Yamamoto, *Solid State Ionics*, 176 (2005) 143-148.
3. K. Amezawa, Y. Kitajima, Y. Tomii and N. Yamamoto, *Electrochem. Solid State Lett.*, 7[12] (2004) A511-A514.
4. H. Onoda, H. Nariai, A. Moriwaki, H. Maki and I. Motooka, *J. Mater. Chem.*, 12[6] (2002) 1754-1760.
5. H. Onoda, T. Ohta, J. Tamaki, K. Kojima and H. Nariai, *Mater. Chem. Phys.*, 96[1] (2006) 163-169.
6. C.-M. Chang, S.-H. Hong and H.-M. Park, *Solid State Ionics*, 176 (2005) 2583-2587.
7. J.L. Xu, K.A. Khor, Y.W. Gu and R. Kumar, P. Cheang, *Biomater.*, 26 (2005) 2197-2207.
8. Y. W.Gu, N.H. Loh, K.A. Khor and S.B. Tor, P. Cheang, *Biomater.*, 23 (2002) 37-43.
9. Y. Kobayashi, T. Takeuchi, M. Tabuchi, K. Ado and H. Kakegawa, *J. Powder Source*, 81-82 (1999) 853-858.
10. T. Onoki, K. Hosoi and T. Hashida, *Scrip. Mater.*, 52 (2005) 767-770.
11. H. Onoda, Y. Inagaki, A. Kuwabara, N. Kitamura, K. Amezawa, A. Nakahira and I. Tanaka, *Phosphorus Res. Bull.*, 23 (2009) 20-24.
12. N. Kitamura, K. Amezawa, Y. Tomii, T. Hanada, N. Yamamoto, T. Omata and S. Otsuka-Yao-Matsuo, *J. Electrochem. Soc.*, 152 (2005) A658-A663.