

Synthesis and Powder Properties of Trivalent Iron Phosphates by the Substitution with Tetravalent Cerium Cation

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Abstract- In this paper, we report the preparation of trivalent iron phosphates in aqueous solution and its use as inorganic yellow pigment. Because cerium phosphate is insoluble in acidic and basic solution, the substitution of cerium cation was tried to improve the acid and base resistance of iron phosphate pigments. The cerium substituted iron phosphates were prepared from phosphoric acid, trivalent iron nitrate, and ammonium cerium nitrate solution. The influence of tetravalent cerium cation was studied on the chemical composition, particle shape and size distribution, specific surface area, color, acid and base resistance of the precipitates and their thermal products. The cerium ratio in precipitates was lower than that in preparation process. Samples had a certain degree of amorphous phase in spite of the Fe/Ce ratio, the addition of H₂O₂, and the heating temperatures. The color of these phosphate pigments was from dark yellow to brownish yellow. The acid resistance of iron phosphate prepared with H₂O₂ improved by the substitution with cerium.

Keywords- Iron Phosphate; Pigment; Cerium Substitution; Acid and Base Resistance

I. INTRODUCTION

Phosphates have been used for ceramic materials, catalysts, fluorescent materials, dielectric substances, metal surface treatment, detergent, food additives, fuel cells, pigments, etc. [1-3]. Especially, as a pigment, these materials have good anticorrosion properties for oxidation reaction and suitable for coating [4-7]. However, there is a weak point that is a certain degree of solubility for acidic and basic solution.

It is well known that rare earth phosphates are insoluble for acidic and basic solution in the groups of phosphate materials. In general, the addition of rare earth elements gives higher functional properties to the material [8]. Consequently, the addition of rare earth cation had the anticipation to improve the acid and base resistances of inorganic phosphate pigments and the other pigmental properties [9-11].

The substitution with lanthanum in nickel and cobalt phosphate materials was studied on the chemical composition, powder condition, color, acid and base resistances in previous works [12, 13]. Specific surface area of phosphates increased and particle size became larger by the substitution with lanthanum. The substitution with lanthanum was effective on acid and base resistance for the design of inorganic phosphate pigments. However, the color of phosphate materials was whitened by the substitution with lanthanum.

Cerium cation is also one of rare earth cations. The

different phenomena are expected with lanthanum cation, because cerium cation has stable tri- and tetra-valent states [14]. Generally, tetravalent cerium cation forms the yellow materials. Therefore, the substitution with tetravalent cerium cation is suitable to improve the acid and base resistance of yellow pigments. In this work, iron (+III) – cerium (+IV) phosphates were synthesized in aqueous solution with and without hydrogen peroxide. The obtained products were estimated from their particle shape and size distribution, specific surface area, color, acid and base resistance.

II. EXPERIMENTAL PROCEDURE

The 0.1 mol/L of iron nitrate, Fe(NO₃)₃, solution was mixed with 0.1 mol/L of phosphoric acid solution in the molar ratio of Fe/P=1/1. This ratio is settled from the chemical composition of iron orthophosphate, FePO₄. The certain part of iron nitrate was substituted with ammonium cerium nitrate, (NH₄)₂Ce(NO₃)₆, in the molar ratio of Fe/Ce=10/0, 8/2, and 5/5 [12, 13]. For the valence balance, four iron cations were replaced by three cerium cations. Totally, the solutions were mixed in the molar ratio of P/(3Fe+4Ce)=1/3. This ratio is corresponding to that phosphate anion is trivalent. To prevent the reduction of iron cation, hydrogen peroxide was added to the molar ratio of Fe/H₂O₂ = 1/1 in the mixed solution. For the comparison, the mixed solution without hydrogen peroxide was also prepared. Then, these mixed solutions were adjusted to pH 7 by ammonia solution. The precipitate was filtered off and dried in air condition. All chemicals were of guaranteed reagents from Wako Chemical Industries Ltd. (Osaka, Japan) without further purification.

A part of the precipitates was dissolved in hydrochloric acid solution. The ratios of phosphorus and cerium in the precipitates were also calculated from ICP results of these solutions, using SPS1500VR, Seiko Instruments Inc. The thermal behavior of these materials was analyzed by TG-DTA and XRD. TG and DTA curves were measured with a Shimadzu DTG-60H at a heating rate of 10°C/min under air. XRD patterns were recorded on a Rigaku Denki RINT 2000 X-Ray diffractometer using monochromated CuK α radiation.

The powder properties of thermal products at 100°C, 200°C, 400°C, and 600°C were characterized by particle shape, particle size distribution, specific surface area, and their color

phase. Particle shapes were observed by scanning electron micrographs (SEM) using JGM-5510LV, JEOL Ltd. Particle size distribution was measured with laser diffraction/scattering particle size distribution HORIBA LA-910. Specific surface areas of phosphates were calculated from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen by BET method with Belsorp mini from BEL JAPAN, INC. The color of phosphate pigments was estimated by ultraviolet - visible (UV-Vis) reflectance spectra with a Shimadzu UV2550.

Furthermore, the acid and base resistances of materials were estimated in following methods. The 0.1 g of thermal products was allowed to stand in 100 ml of 0.1 wt% sulphuric acid or 0.1 wt% sodium hydroxide solution for 1 day. Then, solid was removed off by filtration, the solution was dilute with nitric acid for ICP measurement. The concentrations of phosphorus, iron, cerium were calculated by ICP results. As resistance estimation, the solubility (%) of target elements was calculated to divide by the concentration that thermal products were completely dissolved by hot hydrochloric acid.

III. RESULTS AND DISCUSSION

A. Chemical Composition of Iron – Cerium Phosphates

Table I shows ICP results of samples synthesized in Fe/Ce ratios. From the valence of iron, cerium cations, and phosphate anion, hydrogen ratio was calculated in the following equation.

$$z(\text{hydrogen ratio}) = 3 - 3x(\text{iron ratio}) - 4y(\text{cerium ratio}) \quad (1)$$

The negative value of z means the existence of hydroxide anion. The cerium ratio in the precipitates at Fe/Ce = 8/2 at 5/5 was lower than that of the preparation conditions. In previous works [12, 13], rare earth ratio in precipitates was higher than that in preparation conditions. This phenomenon was caused from that rare earth phosphates have smaller solubility than transition metal phosphates. It is not clear why iron – cerium phosphates had lower cerium ratios. In this work, samples prepared in Fe/Ce=10/0 indicated about 1.15 at Fe/P ratio (x in Table I). Samples prepared with iron (+II) sulfate indicated about 1.65 at Fe/P ratio (manuscript in preparation). The iron resources, iron (+III) nitrate and iron (+II) sulfate, had much influence on Fe/P ratio than the addition of H_2O_2 . Therefore, the oxidation by H_2O_2 was limited to the iron condition in samples.

Figure 1 shows DTA curves of iron – cerium phosphates prepared in various Fe/Ce ratios with and without H_2O_2 . DTA curve of sample prepared in Fe/Ce=10/0 without H_2O_2 had

TABLE I CHEMICAL COMPOSITION, $\text{Fe}_x\text{Ce}_y\text{H}_z\text{PO}_4$, OF SAMPLES PREPARED IN VARIOUS CONDITIONS FROM ICP MEASUREMENTS

Fe/Ce (preparation)	H_2O_2	$\text{Fe}_x\text{Ce}_y\text{H}_z\text{PO}_4$			Fe/Ce (precipitate)
		x	y	z	
10/0	without	1.149	0	-0.477	10/0
8/2	without	1.004	0.180	-0.732	8/1.43
5/5	without	0.633	0.456	-0.723	5/3.60
10/0	with	1.174	0	-0.522	10/0
8/2	with	0.991	0.177	-0.645	8/1.43
5/5	with	1.313	0.470	-2.819	5/1.79

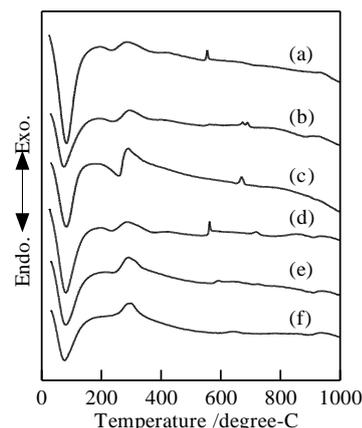


Fig. 1 DTA curves of samples prepared in various Fe/Ce ratios with/without H_2O_2 . (a) 10/0, without H_2O_2 , (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

large endothermic peak at 80°C, small endothermic peak at 230°C, and small exothermic peak at 550°C (Fig.1(a)). These peaks were due to the volatilization of water, dehydration condensation of phosphate, and crystallization of iron phosphate, respectively [12]. The substitution with cerium cation produced the exothermic peaks at 290 and 670°C (Figs. 1(b)(c)). These peaks were related with the reduction of a part of cerium cation and crystallization of cerium phosphate [15]. By the addition of hydrogen peroxide, the endothermic peak at 230°C became small. Samples prepared without H_2O_2 were considered to contain iron hydrogen phosphate anion, HPO_4^{2-} , because this composition changed to condensed phosphate in a following endothermic reaction at 230°C.

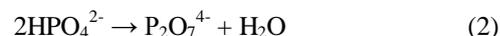


Figure 2 shows TG curves of samples prepared in various Fe/Ce ratios with and without H_2O_2 . The weight losses at 400°C were 52.1, 41.8, 46.2, 46.5, 40.7, and 35.0% from Figure 2(a) to 2(f), respectively. By the substitution with cerium cation, this weight loss became small. Samples prepared without H_2O_2 had the step in TG curves at 230°C (Figs. 2(a)-(c)). This weight loss was considered to be from the condensation reaction of phosphates (2).

Samples prepared in various Fe/Ce ratios with and without H_2O_2 were amorphous in XRD analyses. Figure 3 shows XRD

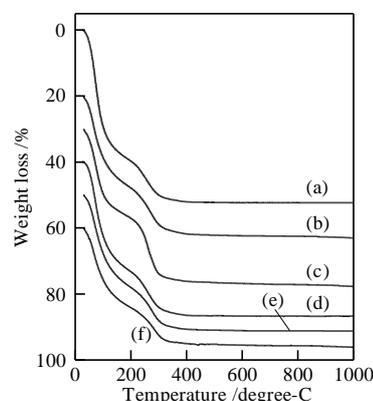


Fig. 2 TG curves of samples prepared in various Fe/Ce ratios with/without H_2O_2 . (a) 10/0, without H_2O_2 , (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

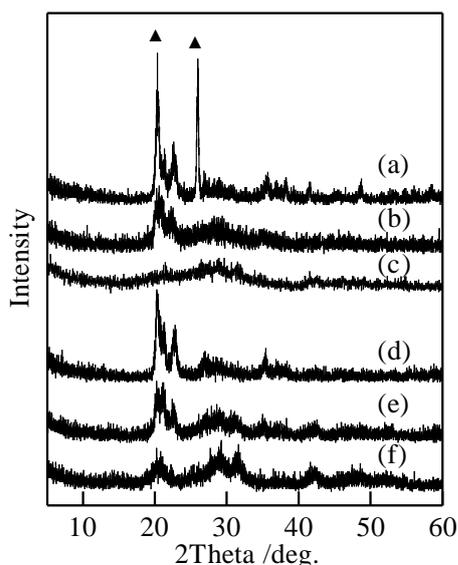


Fig. 3 XRD patterns of samples prepared in various Fe/Ce ratios with/without H_2O_2 and then heated at $600^\circ C$, (a) 10/0, without H_2O_2 , (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with, \blacktriangle ; $FePO_4$ patterns of samples synthesized in various Fe/Ce ratios and then heated at $600^\circ C$. By heating at $600^\circ C$, sample prepared in Fe/Ce=10/0 without H_2O_2 had the peaks of iron phosphate, $FePO_4$. The unknown weak peaks were observed in XRD patterns of all samples. A large part of amorphous phase existed in thermal products at $600^\circ C$.

B. Powder Properties of Iron – Cerium Phosphates

Figure 4 shows SEM images of samples synthesized in

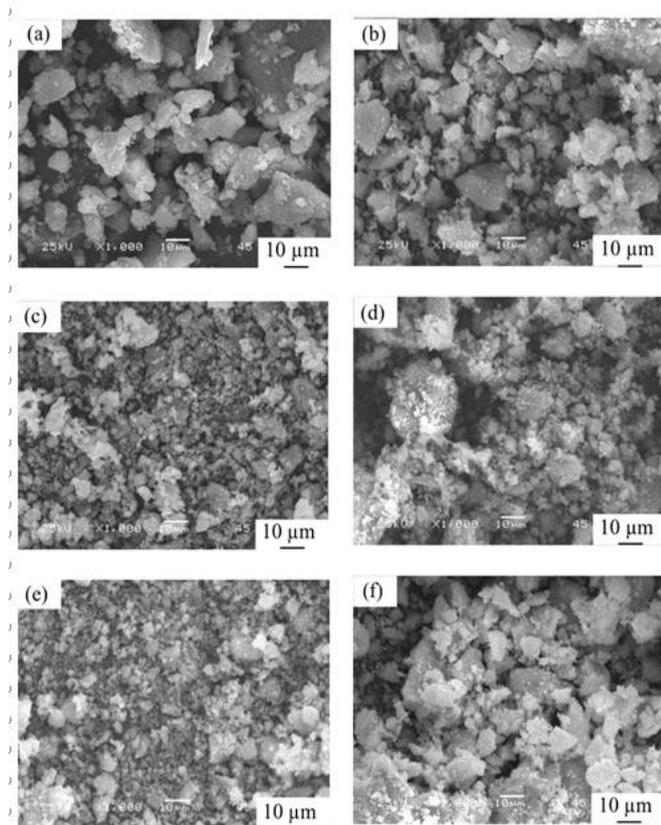


Fig. 4 SEM images of samples prepared in various Fe/Ce ratios with/without H_2O_2 , (a) 10/0, without H_2O_2 , (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

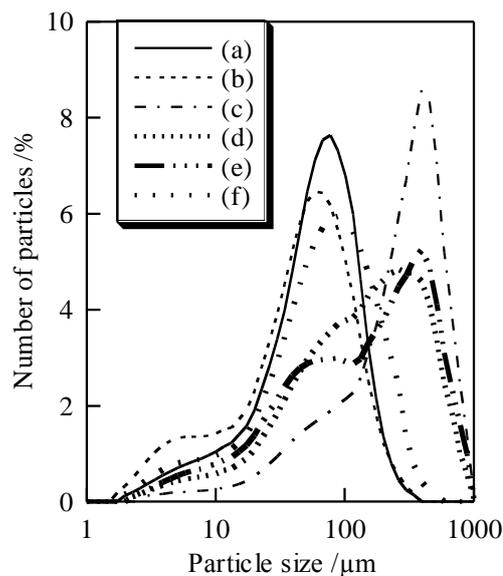


Fig. 5 Particle size distribution of samples prepared in various Fe/Ce ratios with/without H_2O_2 and then heated at $200^\circ C$, (a) 10/0, without H_2O_2 , (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

various Fe/Ce ratios with and without H_2O_2 . Samples had no specified particle shapes in spite of the Fe/Ce ratio and the addition of H_2O_2 . By heating, the particle size became larger. Figure 5 shows the particle size distribution of samples synthesized in various Fe/Ce ratios and then heated at $200^\circ C$. The main part of particle of samples was from 2 to $1000 \mu m$ in size. The influence of Fe/Ce ratios and addition of H_2O_2 was not clear on the particle size distributions. The particle size had little change by heating temperatures.

Table II shows the specific surface area of samples synthesized in various Fe/Ce ratios. Specific surface area as well as particle size has influence on color, and solubility of phosphate materials [16-19]. Samples heated at $200^\circ C$ had large specific surface area. On the other hand, samples heated at $600^\circ C$ had small specific surface area. The Fe/Ce ratio had less influence on specific surface area of samples heated at $200^\circ C$. The decrease of specific surface area by heating was remarkable at samples prepared in Fe/Ce=10/0. Because the particle size of iron phosphates had little change by heating, particles lost the pores on surface by heating at $600^\circ C$. The addition of cerium cation inhibited this decrease of specific surface area.

C. Pigmental Properties of Iron – Cerium Phosphates

The color of samples prepared in various Fe/Ce ratios was from dark yellow to brownish yellow. These colors were less affected from the heating temperatures. These phosphate powders were important not to change colorless powders by heating. In previous works [12, 13], phosphate pigments became white powders by heating. Figure 6 shows UV-Vis reflectance spectra of samples synthesized in various Fe/Ce ratios and then heated at $200^\circ C$. Samples had strong reflectance at 660 nm and weak reflectance at 420 nm. The Fe/Ce ratio and the addition of H_2O_2 had little influence on the color phases of phosphate pigments.

TABLE II SPECIFIC SURFACE AREA OF SAMPLES PREPARED IN VARIOUS CONDITIONS /M² G⁻¹

Fe/Ce (preparation)	H ₂ O ₂	Temperature /°C	
		200	600
10/0	without	118.02	13.35
8/2	without	105.77	21.47
5/5	without	104.66	36.87
10/0	with	121.31	11.24
8/2	with	113.13	25.37
5/5	with	128.68	85.44

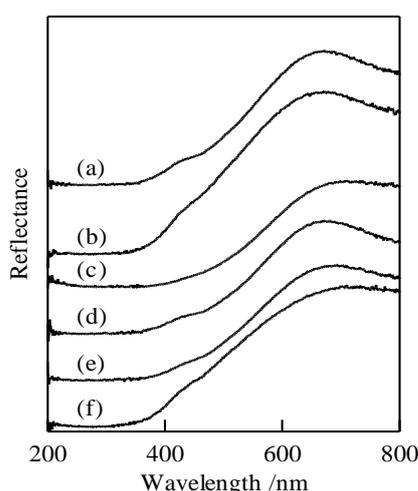
Fig. 6 UV-Vis reflectance spectra of samples prepared in various Fe/Ce ratios with/without H₂O₂ and then heated at 200°C, (a) 10/0, without H₂O₂, (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

Table III shows the eluted ratios of samples prepared in various Fe/Ce ratios with and without H₂O₂ in sulfuric acid. The small number of the eluted ratios means high acid resistance. The eluted ratio of phosphorus at samples prepared with H₂O₂ changed from 93 to 45% with the increase of cerium ratio [20]. Formation of cerium phosphate inhibited the elution of phosphate materials. The elution ratio of iron cation also changed smaller by the substitution with cerium to Fe/Ce=5/5. Figure 7 shows the eluted ratio of phosphorus at samples heated at several temperatures. By heating, the eluted ratios became smaller at all samples. This was caused from the sintering effects. Samples heated at 600°C had small specific surface area and large particles in size (Table II).

Table IV shows the eluted ratios of samples in sodium hydroxide solution. The eluted ratios of iron and cerium cations were small because of the formation of hydroxides. On the other hand, samples had large eluted ratios of phosphorus. The substitution with cerium had less influence on base resistance.

TABLE III ELUTED RATIO OF SAMPLES IN SULFURIC ACID SOLUTION /%

Fe/Ce	H ₂ O ₂	P	Fe	Ce
10/0	without	72.9	71.2	-
8/2	without	100	100	62.6
5/5	without	67.5	71.5	60.3
10/0	with	93.1	88.8	-
8/2	with	51.2	46.9	11.9
5/5	with	45.4	35.4	11.5

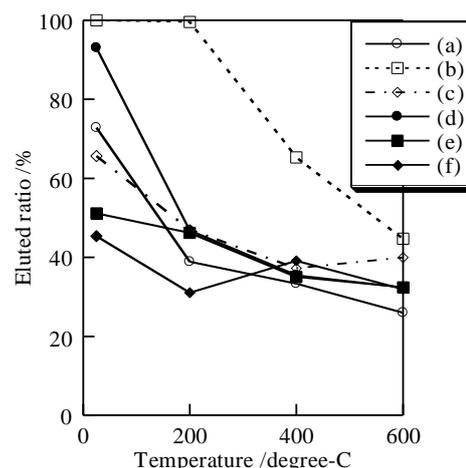
Fig. 7 Eluted ratio of phosphorus in sulfuric acid solution at samples prepared in various Fe/Ce ratios with/without H₂O₂ and then heated at several temperatures, (a) 10/0, without H₂O₂, (b) 8/2, without, (c) 5/5, without, (d) 10/0, with, (e) 8/2, with, and (f) 5/5, with

TABLE IV ELUTED RATIO OF SAMPLES IN SODIUM HYDROXIDE SOLUTION /%

Fe/Ce	H ₂ O ₂	P	Fe	Ce
10/0	without	76.6	1.4	-
8/2	without	100	1.8	0.6
5/5	without	64.9	0.1	0.2
10/0	with	84.7	23.7	-
8/2	with	100	3.9	3.4
5/5	with	89.8	0.9	0.9

IV. CONCLUSIONS

In summary, iron-cerium phosphates were prepared in aqueous solution. The obtained products were estimated for design of functional materials. The cerium ratio in precipitates was lower than that in preparation process. Samples had a certain degree of amorphous phase in spite of the Fe/Ce ratio, the addition of H₂O₂, and the heating temperatures. The color of these phosphate pigments was from dark yellow to brownish yellow. The acid resistance of iron phosphate prepared with H₂O₂ improved by the substitution with cerium.

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