

Influence of lanthanum addition on preparation and powder properties of cobalt phosphates

Hiroaki Onoda · Keisuke Tange · Isao Tanaka

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Abstract Transition metal phosphates are used as inorganic pigments; however, these materials had a weak point for acid and base resistance. Because lanthanum phosphate is insoluble in acidic and basic solution, the addition of lanthanum cation was tried to improve the acid and base resistance of cobalt phosphate pigment. The lanthanum doped cobalt phosphates were prepared from phosphoric acid, cobalt nitrate, and lanthanum nitrate solution. The additional effects of lanthanum cation were 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.

Introduction

Phosphates have been used for ceramic materials, catalysts, fluorescent materials, dielectric substances, metal surface treatment, detergent, food additives, fuel cells, pigments,

etc. [1–4]. Especially, as a pigment, these materials have good anticorrosion properties and suitable for coating [5–8]. 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 [9]. Consequently, the addition of rare earth cation had the anticipation to improve the acid and base resistance of inorganic phosphate pigments. In previous works, the addition of rare earth cation were studied in solid state syntheses and powder properties, acid and base resistance of cobalt, copper, nickel, manganese ortho-, pyro-, and *cyclo*-tetra-phosphates [3, 4, 10]. The chemical composition and powder properties of thermal products were changed by the addition of rare earth cation. Furthermore, this addition improved the acid and base resistance of phosphate materials synthesized in solid state reaction.

For the syntheses of inorganic phosphates, there are some methods, one is based on the solid state reaction, another one is on the cation exchange reaction in aqueous solution, and others. The method by the solid state reaction had some merits to be easy to form condensed phosphate and to control the molar ratio of cation/phosphorus, on the other hand, had a demerit to be difficult to keep the homogeneity of materials. The preparation of transition metal phosphate in aqueous solution had an advantage to obtain the homogenized materials and various kinds of metal phosphates. However, it had a weak point to be difficult to control the molar ratio of cation/phosphorus. The synthetic method had much influence on the properties of phosphate materials. There are some cases that the phosphate prepared in aqueous solution has the different properties with the phosphate synthesized in solid state

H. Onoda (✉)
Department of Environment and Information Sciences, Faculty of Life and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-cyo, Sakyo-ku, Kyoto 606-8522, Japan
e-mail: onoda@kpu.ac.jp

K. Tange
Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga 525-8577, Japan

I. Tanaka
Department of Materials Science and Engineering, Faculty of Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

reaction. It is important to clear the additional effects of rare earth cation on syntheses of inorganic phosphate materials prepared in wet process and their properties.

In this work, the lanthanum doped cobalt phosphates were prepared from phosphoric acid, cobalt nitrate, and lanthanum nitrate solution. The thermal behavior of these precipitations was investigated, and then their thermal products were estimated from their particle shape and size distribution, specific surface area, color, acid and base resistance.

Experimental

Cobalt nitrate solution (0.1 mol/L) was mixed with 0.1 mol/L of phosphoric acid solution in the molar ratio of Co/P = 3/2. This ratio is settled from the chemical composition of cobalt orthophosphate, $\text{Co}_3(\text{PO}_4)_2$. Certain part of cobalt nitrate was substituted with lanthanum nitrate in the molar ratio of La/Co = 0/10, 1/9, 2/8, 5/5, 8/2, and 10/0 [11, 12]. For the valence balance, three cobalt cations were replaced with two lanthanum cations. Finally, the solutions were mixed in the molar ratio of La/P = 1/1. These preparation ratios are shown in Table 1. Then, the mixed solution was adjusted to pH 7 by ammonia solution. The precipitation was filtered off and dried in air condition. A part of the precipitate was dissolved in hydrochloric acid solution. The ratios of cobalt, lanthanum, phosphorus in the precipitate were calculated from inductivity coupled plasma-atomic emission spectrometry (ICP) results of these solutions. The ICP estimation was measured with Shimadzu ICPS-8000.

The thermal behavior of these precipitations was analyzed by thermogravimetry-differential thermal analyses

(TG-DTA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). TG and DTA curves were measured with a Shimadzu DTA-60/60H at a heating rate of 10 °C/min under air condition. X-ray diffraction patterns were recorded on a Rigaku Denki RINT2000M X-Ray diffractometer using monochromated $\text{CuK}\alpha$ radiation. The IR spectra were recorded on a Shimadzu FT-IR spectrometer FT-IR8600 with a KBr disk method.

The powder properties of thermal products at 200 °C, 400 °C, 600 °C, and 800 °C were characterized by particle shape, particle size distribution, specific surface area, and their color. Particle shapes were observed by scanning electron micrographs (SEM) using VE8800 from Keyence Co. 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 Bel-sorp mini from BEL JAPAN, INC. The color of phosphate pigments was estimated by ultraviolet–visible (UV–Vis) reflectance spectra with a Shimadzu UV368.

Furthermore, the acid and base resistance of materials was estimated by the following method. Thermal products (0.1 g) were allowed to stand in 100 mL of 0.1 wt% sulfuric acid or 0.1 wt% sodium hydroxide solution for 1 day. Then, solid was removed off by filtration; the solution was diluted with nitric acid for ICP measurement. The concentrations of phosphorus, cobalt, lanthanum cation were calculated by ICP results. For resistance estimation, the elution ratio (%) of target elements was calculated to divide by the concentration that thermal products were completely dissolved by hot hydrochloric acid.

Results and discussion

Chemical composition and thermal behavior of the precipitations

Table 1 The relationship between the preparation ratio and chemical composition of precipitations from ICP results

La/Co	$\text{Co}_x\text{La}_y\text{H}_z\text{PO}_4$					
	Preparation ratio ^a			Precipitation ratio ^b		
	x	y	z	x	y	z
0/10	3/2	0	–	1.398	0	0.203
1/9	9/7	1/7	–	1.515	0.165	–0.525
2/8	12/11	3/11	–	1.055	0.296	0.003
5/5	3/5	3/5	–	0.488	0.644	0.090
8/2	3/14	12/14	–	0.185	0.919	–0.126
9/1	3/29	27/29	–	0.047	0.964	0.014
10/0	0	1	–	0	0.867	0.400

^a All conditions had the preparation ratios of Co/P = 3/2 and La/P = 1/1

^bFor the valence balance, $2x(\text{cobalt}) + 3y(\text{lanthanum}) + z(\text{hydrogen}) = 3(\text{phosphate})$ in precipitation ratio

Table 1 shows the ratios of cobalt, lanthanum, and phosphorus in the precipitate from ICP results. In this table, x and y are the ratios of Co/P and La/P, respectively. Sample prepared at La/Co = 0/10 had Co/P = 1.398. The major composition was $\text{Co}_3(\text{PO}_4)_2$ and minor one was CoHPO_4 (NH_4CoPO_4). In the condition where z values were negative in this table, cobalt and lanthanum hydroxides were co-precipitated with phosphates. Cobalt–lanthanum phosphate had smaller hydrogen ratio than nickel–lanthanum phosphate [13]. LaPO_4 was considered to be form in lanthanum-rich condition. Figure 1 shows the relationship between the preparation and precipitation ratios of cobalt and lanthanum. The precipitation had similar lanthanum ratio with the ratio in preparation process.

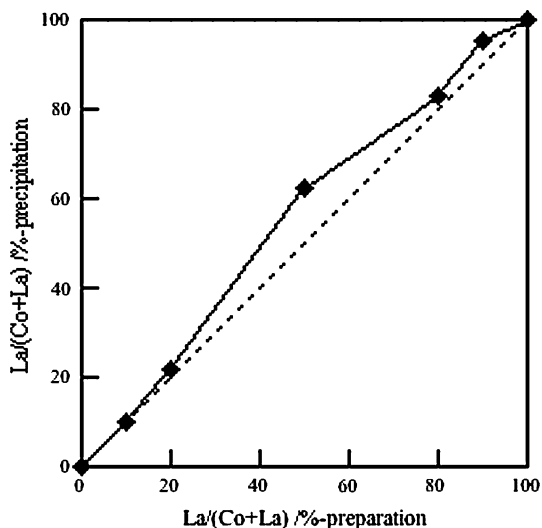


Fig. 1 Relationship between the lanthanum ratio, $La/(La + Co)$, of the preparation conditions and that in the precipitations

Figure 2 shows TG curves of cobalt-lanthanum phosphates. Cobalt phosphate had larger weight loss than others (Fig. 2a). The weight loss consisted of some steps, they were considered to be from the volatilization of adsorbed water, crystalline water, ammonia from NH_4CoPO_4 , the condensation water from $CoHPO_4$ to $Co_2P_2O_7$. The calculated weight losses of the volatilization of ammonia from NH_4CoPO_4 and the condensation water from $CoHPO_4$ to $Co_2P_2O_7$ were 7.9% and 4.2%, those in experimental result were 11.2% and 4.6%. The weight loss of sample in $La/Co = 10/0$ was larger than that of sample in $La/Co = 8/2$, because sample in La/Co had more amount of adsorbed water. Figure 3 indicates DTA curves of cobalt-lanthanum phosphate. Some endothermic peaks were observed in DTA curve of sample prepared at $La/Co = 0/10$. It is difficult to

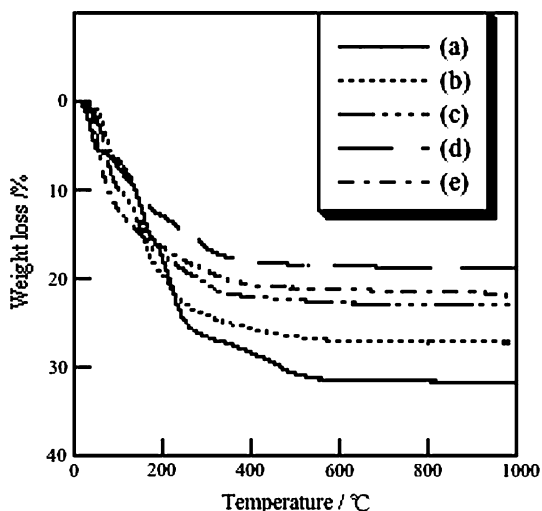


Fig. 2 TG curves of samples prepared at various La/Co ratios, (a) $La/Co = 0/10$, (b) $2/8$, (c) $5/5$, (d) $8/2$, and (e) $10/0$

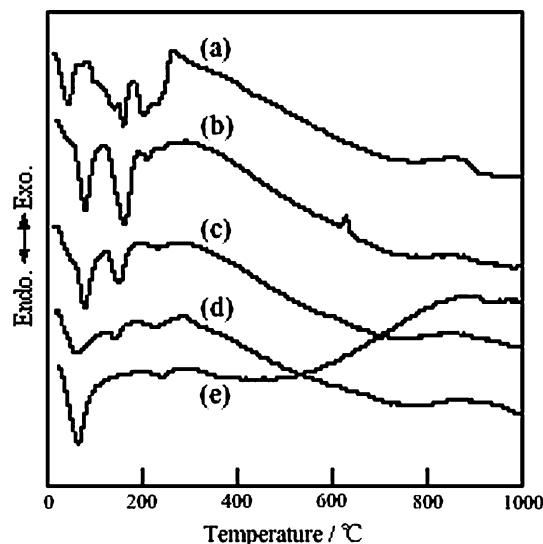


Fig. 3 DTA curves of samples prepared at various La/Co ratios, (a) $La/Co = 0/10$, (b) $2/8$, (c) $5/5$, (d) $8/2$, and (e) $10/0$

clear the cause of these peaks. However, the endothermic peaks at about 80 °C and 160 °C in DTA curve of sample at $La/Co = 2/8$ were considered to be due to the volatilization of water and ammonia. With the increase of lanthanum ratio, these endothermic peaks became small. IR spectra of precipitations are shown in Fig. 4. Sample prepared at $La/Co = 0/10$ had the adsorption peaks due to water, ammonium, nitrate ion, and phosphate. The spectrum changed gradually with the lanthanum ratio. Sample prepared at $La/Co = 10/0$ indicated the peaks of Rhabdophane-type $LaPO_4$ with the peak of nitrate anion. Figure 5 shows XRD patterns of samples heated at 800 °C. Sample at $La/Co = 0/10$ had the peaks of $Co_3(PO_4)_2$ and $Co_2P_2O_7$. On the other hand, the

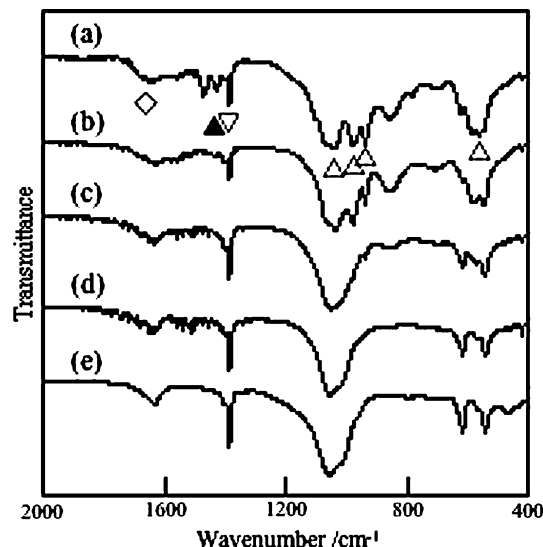


Fig. 4 IR spectra of samples prepared at various La/Co ratios (R.T.), (a) $La/Co = 0/10$, (b) $2/8$, (c) $5/5$, (d) $8/2$, and (e) $10/0$, Δ ; P–O and/or P = O, \diamond ; H_2O , ∇ ; NO_3^- , and \blacktriangle ; NH_4^+

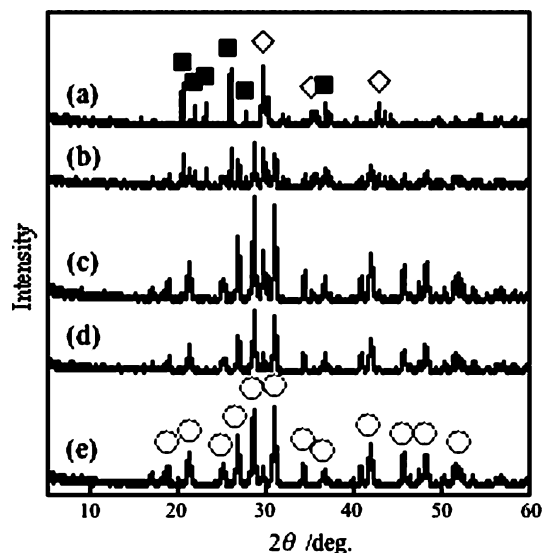


Fig. 5 XRD patterns of samples prepared at various La/Co ratios and heated at 800 °C, (a) La/Ni = 0/10, (b) 2/8, (c) 5/5, (d) 8/2, and (e) 10/0, ■; $\text{Co}_3(\text{PO}_4)_2$, ◇; $\text{Co}_2\text{P}_2\text{O}_7$, ○; LaPO_4

peaks of Monazite-type LaPO_4 were observed in sample at La/Co = 10/0.

The precipitates prepared at La/Co = 0/10 was a mixture of $\text{Co}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ and $\text{NH}_4\text{CoPO}_4 \cdot n\text{H}_2\text{O}$. By the addition of lanthanum cation, Rhabdophane-type LaPO_4 was precipitated. Ammonium cobalt phosphate, $\text{NH}_4\text{CoPO}_4 \cdot n\text{H}_2\text{O}$, was changed to CoHPO_4 losing the crystalline water and ammonia by heating. Then, cobalt hydrogen

phosphate, CoHPO_4 , was condensed to $\text{Co}_2\text{P}_2\text{O}_7$ by losing the structural water. Totally, the sample in La/Co = 0/10 at 800 °C was the mixture of $\text{Co}_3(\text{PO}_4)_2$ and $\text{Co}_2\text{P}_2\text{O}_7$. On the other hand, Rhabdophane-type LaPO_4 changed to Monazite-type LaPO_4 by heating. The samples prepared between La/Co = 1/9 and 9/1 were the mixture of cobalt and lanthanum phosphates in chemical composition.

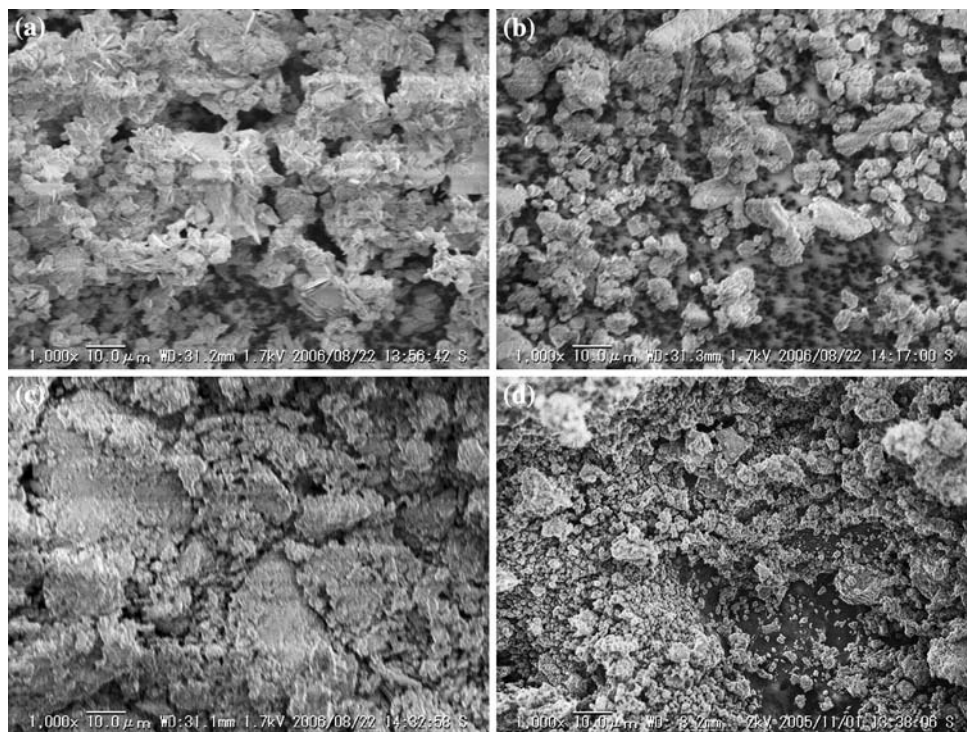
Powder properties of thermal products

Figure 6 shows SEM images of samples heated at 200 °C. All samples in this work had no specified shape in spite of La/Co ratio and heating temperature. Figure 7 shows particle size distribution of samples heated at 200 °C. The large part of sample at La/Co = 0/10 was from 2 to 200 μm in size. Samples at La/Co = 8/2 and 10/0 consisted of larger particle than samples with high cobalt ratio. The same tendency was observed in particle size distribution of samples heated at higher temperatures. Table 2 shows specific surface area of cobalt–lanthanum phosphate. Samples at La/Co = 0/10 had small specific surface area, on the other hand, those at La/Co = 10/0 was large one. Specific surface area increased with lanthanum ratio. By heating, specific surface area of samples in all ratios became small.

Color of precipitations and their thermal products

As an inorganic pigment, the hue of materials is important. The precipitate at La/Co = 0/10 without heating was

Fig. 6 SEM images of samples prepared at various La/Co ratios and heated at 200 °C, (a) La/Ni = 0/10, (b) 2/8, (c) 8/2, and (d) 10/0



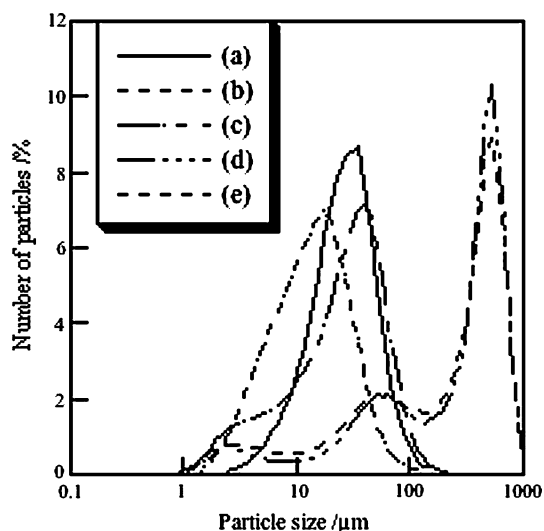


Fig. 7 Particle size distribution of samples prepared at various La/Co ratios and heated at 200 °C, (a) La/Ni = 0/10, (b) 2/8, (c) 5/5, (d) 8/2, and (e) 10/0

Table 2 Specific surface area of cobalt–lanthanum phosphates/ $\text{m}^2 \text{g}^{-1}$

La/Co	Temperature/°C			
	200	400	600	800
0/10	3.61	5.23	6.01	2.73
1/9	26.24	26.52	12.61	2.64
2/8	21.77	23.91	10.97	2.46
5/5	67.27	68.36	24.56	3.93
8/2	101.57	98.88	50.29	7.58
9/1	84.97	102.77	58.84	3.56
0/0	100.97	101.90	43.69	8.16

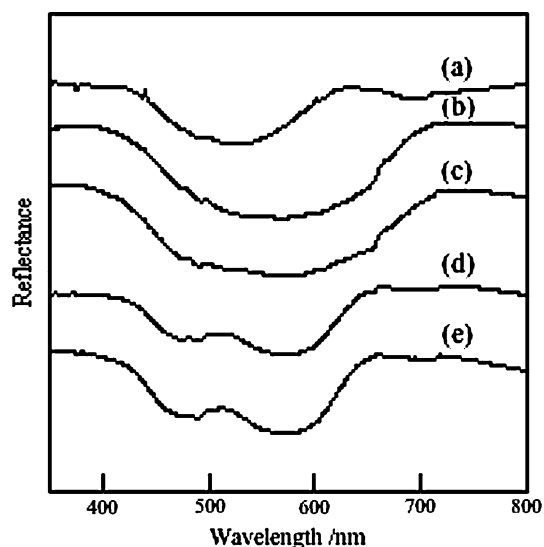


Fig. 8 UV–Vis reflectance spectra of samples prepared at La/Co = 0/10, (a) R.T., (b) 200 °C, (c) 400 °C, (d) 600 °C, and (e) 800 °C

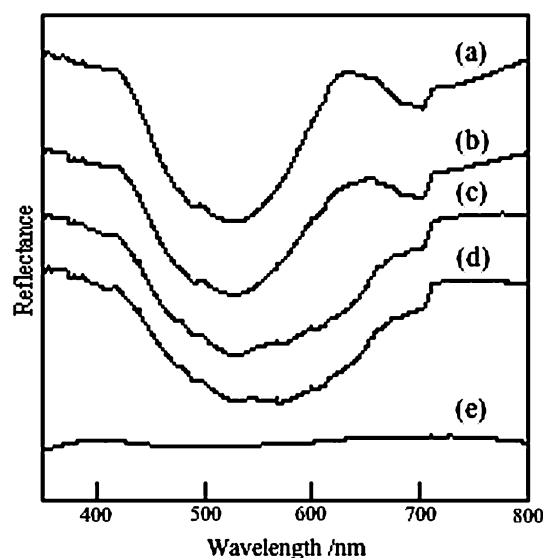


Fig. 9 UV–Vis reflectance spectra of samples prepared at various La/Co ratios (R.T.), (a) La/Co = 0/10, (b) 2/8, (c) 5/5, (d) 8/2, and (e) 10/0

reddish purple. By heating at 200 °C and 400 °C, the color of samples changed blue [14], and samples heated at 600 °C and 800 °C were violet in color. Figure 8 shows UV–Vis reflectance spectra of samples at La/Co = 0/10 heated at several temperatures. The spectrum of precipitation without heating had broad peak at 530 nm. This peak shifted to longer wavelength by heating at 200 °C and 400 °C. Samples heated at 600 °C and 800 °C indicated different spectra, which had the peaks at 470, 490, 580 nm in wavelength. Figure 9 shows UV–Vis reflectance spectra of samples prepared at various La/Co ratios (without heating). By the addition of lanthanum cation, the peaks broadened, and finally disappeared. The color of samples

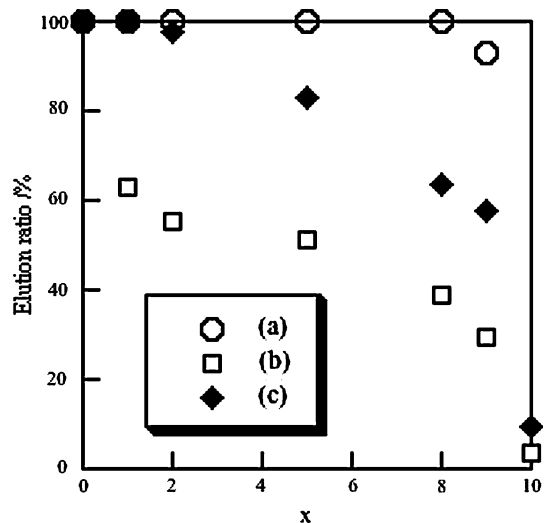


Fig. 10 Acid resistance of samples prepared at La/Co = $x/(10 - x)$ and heated at 200 °C, (a) Co, (b) La, and (c) P

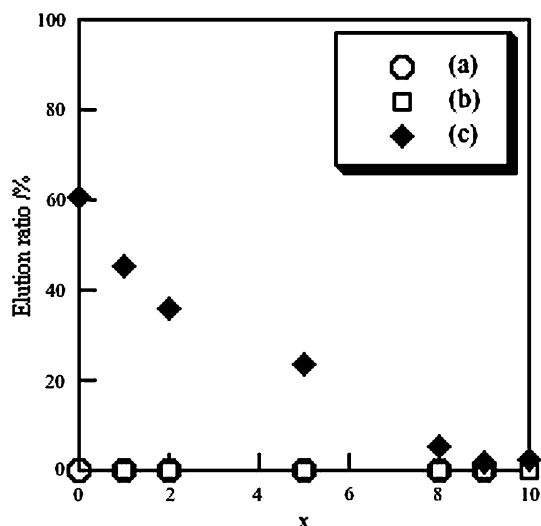


Fig. 11 Base resistance of samples prepared at $\text{La/Co} = x/(10 - x)$ and heated at 200 °C, (a) Co, (b) La, and (c) P

was whitened with the increase of lanthanum ratio. The heating temperature and the La/Co ratios had influence on the hue of cobalt–lanthanum phosphate.

Acid and base resistance estimation of phosphates

Figure 10 shows acid resistance of samples heated at 200 °C. Cobalt ion indicated high elution ratio for acid solution in spite of lanthanum ratio. The acid resistance of lanthanum and phosphorus improved with the increase of lanthanum ratio. Samples became difficult to elute by heating at high temperatures.

Figure 11 shows base resistance of samples heated at 200 °C. Cobalt and lanthanum ions indicated no elution, because these were precipitated as their hydroxides. The elution ratio of phosphorus was decreased by the addition of lanthanum. Base resistance also improved by heating at higher temperature.

Conclusion

The substitution by lanthanum in cobalt phosphate materials were studied on the chemical composition, powder

condition, color, acid and base resistance. Lanthanum phosphate was formed with cobalt phosphates. Thermal behavior of precipitations changed gradually with increase of lanthanum ratio. Specific surface area of phosphates increased and particle size became larger by the addition of lanthanum. The color of cobalt phosphate was changed by heating and whitened by the addition of lanthanum. The substitution by lanthanum on acid and base resistance was effective for design of inorganic phosphate pigment.

References

1. Onoda H, Nariai H, Moriwaki A, Maki H, Motooka I (2002) *J Mater Chem* 12(6):1754. doi:10.1039/b110121h
2. Onoda H, Ohta T, Tamaki J, Kojima K (2005) *Appl Catal Gen* 288(1–2):98. doi:10.1016/j.apcata.2005.04.028
3. Onoda H, Yokouchi K, Kojima K, Nariai H (2005) *Mater Sci Eng B* 116(2):189. doi:10.1016/j.mseb.2004.10.002
4. Onoda H, Kojima K, Nariai H (2006) *J Alloys Comp* 408–412:568
5. Lenz DM, Delamar M, Ferreira CA (2007) *Prog Org Coat* 58:64. doi:10.1016/j.porgcoat.2006.12.002
6. Mahdavian MA, Attar MM (2005) *Electrochim Acta* 50:4645. doi:10.1016/j.electacta.2005.02.015
7. Hernandez MA, Galliano F, Landolt D (2004) *Corros Sci* 46:2281. doi:10.1016/j.corsci.2004.01.009
8. Deya MC, Blustein G, Romagnoli R, del Amo B (2002) *Surf Coat Tech* 150:133. doi:10.1016/S0257-8972(01)01522-5
9. Topp NE (1974) In: Shiohawa J, Adachi G (eds) *Chemistry of the rare earth elements*, Kagakudojin, Kyoto, p 184
10. Onoda H, Nariai H, Maki H, Motooka I (2001) *Phosphorus Res Bull* 12:139
11. Onoda H, Ohta T, Tamaki J, Kojima K, Nariai H (2006) *Mater Chem Phys* 96(1):163. doi:10.1016/j.matchemphys.2005.07.001
12. Onoda H, Sugino N, Kojima K, Nariai H (2003) *Mater Chem Phys* 82(3):831. doi:10.1016/j.matchemphys.2003.07.006
13. Onoda H, Matsui H, Tanaka I (2007) *Mater Sci Eng B* 141(1–2):28. doi:10.1016/j.mseb.2007.05.009
14. Mesegure S, Tena MA, Gargori C, Badenes JA, Llusar M, Monros G (2007) *Ceram Int* 33:843. doi:10.1016/j.ceramint.2006.01.024