Synthesis and Characterization of New Environmentally-Friendly Pigments Based on Cerium Phosphate

Toshiyuki MASUI, Hiroshi TATEGAKI, Shinya FURUKAWA and Nobuhito IMANAKA

Department of Applied Chemistry, Faculty of Engineering and Handai Frontier Research Center, Osaka University,
2-1, Yamadaoka, Suita-shi, Osaka 565-0871

リン酸セリウムを母体とする新しい環境調和型顔料の合成とキャラクターゼーション

増井敏行・立垣裕史・古川慎也・今中信人

大阪大学大学院工学研究科物質化学専攻, 565-0871 大阪府吹田市山田丘 2-1

New yellow-green pigments based on cerium orthophosphate were synthesized by the solid-state reaction in order to develop ecological and environmentally-friendly specific pigments. The pigments were obtained by doping alkaline earth metal ions into a cerium orthophosphate lattice to form their solid solutions. The products were characterized by using X-ray powder diffraction, UV-Vis spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, and colorimetric assessment. From these results, it has been evidenced that the formation of solid solution is necessary to have color coordinates in the synthesized pigment samples. Since the color of the pigments was almost the same yellow-green in all solid solution samples, the origin of the coloration was attributed to the appearance of the principal broad absorption band corresponding to the 4f–5d electron transition of Ce^{3+} and the additional O_{2p} – Ce_{4f} charge transfer transition of Ce^{4+} by the doping of alkaline earth ion into CePO_4 lattice.

[Received August 10, 2004; Accepted October 26, 2004]

Key-words: Cerium phosphate, Solid solution, Ecological pigments, Color properties, FT-IR, Raman spectroscopy

1. Introduction

Inorganic pigments have been applied in various applications such as paints, ceramics, plastics, enamels, glasses, and so on.¹⁾ However, the conventional inorganic pigments for the above applications contain the toxic elements such as Cd, Co, Cr, Hg, Pb, Sb, or Se. Therefore, discovery and development of new and improved inorganic pigments have been desired in order to replace toxic inorganic pigments with more environmentally-friendly pigments or less toxic substances. Although the use of high-performance organic pigments is one way to get several colors, these pigments have some limitations because of thermal and ultraviolet (UV)-ray radiation instabilities. As a work on this line, some new safe inorganic pigments based on metal oxides and compounds have been proposed by several researchers including our group.^{2)–6)} However, only a few new inorganic pigments have been developed in recent decades.

In the present study, new pigments based on cerium orthophosphate have been synthesized and their color properties have been investigated from the viewpoint of possible ecological inorganic pigments. Cerium phosphate (CePO_4) is a well-known material that exists in nature as a main component of Monazite minerals and very stable against heat and UV-rays. The pigments presented in this study are inert and safe not to give side effects to the human body, because metal phosphate is a main component of bone and tooth. These pigments can be prepared by a simple solid-state reaction method using the starting materials containing non-toxic elements, and the optical and color properties of CePO_4 based pigments have been characterized.

2. Experimental

The starting materials used for the synthesis of CePO_4 -based pigments were CePO_4 (High Purity Chemicals, 99.9%),

MgCO_3 (Wako Chemicals, 99.99%), CaCO_3 (Wako Chemicals, 99.99%), SrCO_3 (Wako Chemicals, 99.99%), BaCO_3 (Wako Chemicals, 99.9%), $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$ (Wako Chemicals, 97%), and $(\text{NH}_4)_2\text{HPO}_4$ (Aldrich, 99.99%). These materials were thoroughly mixed in a molar ratio of $\text{CePO}_4 : \text{MCO}_3 : (\text{NH}_4)_2\text{HPO}_4 = 9 : 1 : 1$ ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{and Zn}$) in an agate mortar for 30 min. The mixtures were calcined at 900°C for 12 h in air atmosphere in an electric resistance furnace increasing the temperature at a rate of 3°C min^{−1}. In order to identify the effect of the existence of a 4f electron in the host phosphate to the hue of the pigments, Ca-, Sr-, and Ba-doped LaPO_4 pigments were also synthesized as reference samples in the same procedure for the CePO_4 -based samples.

The pigments were characterized by X-ray powder diffraction (XRD; Rigaku, Multiflex). The XRD patterns were recorded in the 2θ range from 10° to 70° using $\text{Cu K}\alpha$ radiation. Optical reflectance, FT-IR, and Raman spectra of the powder were measured with a UV-Vis spectrometer (Shimadzu UV-2450) using barium sulfate as a reference, an FT-IR spectrometer (Bruker TENSOR27), and a Raman spectrometer (Kaiser Optical Systems, Inc., Holoprobe), respectively.

The color properties of the samples were estimated in terms of CIE $L^*a^*b^*$ system with a colorimeter (Minolta, CR-300). The values a^* (the axis red-green) and b^* (the axis yellow-blue) indicate the color hue. The value L^* represents the lightness or darkness of the color as related to a neutral grey scale. In the $L^*a^*b^*$ system, it is described by numbers from zero (black) to 100 (white).

3. Results and discussion

Figure 1 presents the X-ray powder diffraction results of the alkaline earth-doped CePO_4 pigments in comparison with that of pure CePO_4 . The single solid solution phase of

Fig. 1. X-ray powder diffraction patterns of (a) pure, (b) Mg-doped, (c) Ca-doped, (d) Sr-doped, (e) Ba-doped, and (f) Zn-doped CePO_4 samples.

CePO_4 was obtained when Ca, Sr, or Ba was doped. The CePO_4 has a monazite-type monoclinic crystal structure^(7),8) and the pattern shifted to higher angle by the Ca doping without any phase decompositions, while to lower angle by the Sr or Ba doping. Because the ionic radius of Ce^{3+} (0.120 nm for 9-coordinate⁹⁾) is larger than that of Ca^{2+} (0.118 nm for 9-coordinate⁹⁾) and is smaller than those of Sr^{2+} (0.131 nm for 9-coordinate⁹⁾) and Ba^{2+} (0.147 nm for 9-coordinate⁹⁾), the X-ray results explicitly show that solid solutions were successfully obtained as a single phase by the replacement of the Ce^{3+} site for these ions. In contrast, in the cases for the Mg and Zn doping, no peak shift was observed in their XRD patterns and $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Zn}_3(\text{PO}_4)_2$ were produced as the secondary phases, respectively.

The XRD patterns for the reference LaPO_4 -based pigments are shown in Fig. 2 with that of pure LaPO_4 . Similar results to the CePO_4 pigments were obtained, because the ionic radius of La^{3+} (0.122 nm for 9-coordinate⁹⁾) is also larger than that of Ca^{2+} and is smaller than those of Sr^{2+} and Ba^{2+} .

The color drastically changed from white to yellow-green by forming the solid solutions of Ca-, Sr-, and Ba-doped CePO_4 . The effect of alkaline earth doping on the color of the CePO_4 based pigments was analyzed from the diffuse reflectance spectra depicted in Fig. 3. The Mg or Zn doping, because solid solutions are not produced with these dopants, did not affect the reflectance spectrum of CePO_4 . However, the reflectance spectra of the Ca-, Sr-, Ba-doped CePO_4 shows a strong absorption band under 500 nm and a relatively small and

Fig. 2. X-ray powder diffraction patterns of (a) pure, (b) Ca-doped, (c) Sr-doped, and (d) Ba-doped LaPO_4 solid solutions.

Fig. 3. Reflectance spectra for CePO_4 -based pigments.

broad peak at 600–650 nm, compared with that of pure CePO_4 . These peaks imply some variation of the crystal field strength by the solution of alkaline metal ions into the CePO_4 lattice. The change of the relative reflection intensities is responsible for the color change.

The $L^*a^*b^*$ color coordinate data of pure CePO_4 and the Mg-, Ca-, Sr-, Ba-, and Zn-doped CePO_4 pigments are summarized in Table 1. In this system, the L^* values are indicative of color lightness, while a^* and b^* represent the level of red-green and yellow-blue components, respectively. As seen in Table 1,

Table 1. Color Coordinate Values of the Pigments in the $L^*a^*b^*$ System

Sample	L^*	a^*	b^*	Color
pure CePO_4	95.5	-0.54	+1.25	white
Mg-doped CePO_4	96.0	-0.54	+1.67	white
Ca-doped CePO_4	72.9	-8.08	+13.7	yellow-green
Sr-doped CePO_4	73.4	-8.91	+15.9	yellow-green
Ba-doped CePO_4	68.1	-8.30	+14.1	yellow-green
Zn-doped CePO_4	97.2	-0.53	+1.96	white
Pure LaPO_4	98.0	-0.02	+0.12	white
Ca-doped LaPO_4	99.7	-0.47	+1.22	white
Sr-doped LaPO_4	99.5	-0.20	+0.60	white
Ba-doped LaPO_4	99.1	-0.36	+0.92	white

Fig. 4. Absorbance spectra of (a) pure CePO_4 and (b) Ca-, Sr-, or Ba-doped CePO_4 pigments.

L^* and a^* decreased but b^* increased by the formation of solid solutions with alkaline earths, indicating that the CePO_4 -based solid solution pigments have medium color lightness with the enhancement of green and yellow color. These results correspond to the above optical reflectance results.

The absorbance spectra of the white CePO_4 and the yellow-green Ca-, Sr-, or Ba-doped CePO_4 pigments represented with the remission function, $f(R) = (1 - R)^2/2R$, are depicted in Fig. 4, where R is reflectance.^{10),11)} The weak absorption peaks are observed at 273 and 292 nm in pure CePO_4 . By the formation of solid solutions with alkaline earths, the peak at 273 nm splits into 259 and 273 nm and the intensity was drastically enhanced (compare the ordinate in Figs. 4(a) and (b)) and the peak at 292 nm shifted to longer wavelength (337 nm) with tailing its edge to 450 nm. The magnitude of the enhancement of the former peaks was bigger than the latter. In addition, a new weak absorption peak appeared around 600–650 nm in every sample (the inset in Fig. 4(b)). Absorptions of the visible light at around 400–450 (purple) and yellow and 600–650 nm (red) correspond to the appearance of yellow and green colors, respectively, because yellow is a complementary color to blue and green is the one to red.

In the case of LaPO_4 -based pigments, in contrast, the color almost unchanged even if the solid solutions were produced by the Ca, Sr, and Ba doping, as seen in the reflectance spectra in Fig. 5. The $L^*a^*b^*$ color coordinate data of the LaPO_4 -based pigments are also summarized in Table 1. Contrary to the results for the CePO_4 -based pigments, no effect is observed in their optical spectra and hue by the formation of the LaPO_4 solid solutions with the alkaline earth ions. In order to identify a mechanism of the color appearance, FT-IR and Raman spectra for the CePO_4 - and LaPO_4 -based pigments were characterized as shown in Figs. 6 and 7, respectively.

In the FT-IR spectra, the bands around 1110 (shoulder), 1092, 1070, 1020, 995, 954 (sharp), 627, 575, 560, and 538 cm^{-1} are assigned to the PO_4 group in rare earth or-

Fig. 5. Reflectance spectra for LaPO_4 -based solid solutions. Fig. 6. FT-IR spectra of (a) Ca-doped LaPO_4 , (b) LaPO_4 , (c) Ca-doped CePO_4 , and (d) CePO_4 . Fig. 7. Raman spectra of (a) Sr-doped LaPO_4 , (b) Sr-doped CePO_4 , (c) Ca-doped LaPO_4 , and (d) Ca-doped CePO_4 .

thophosphates.^{12),13)} The bands at 1110, 1092, 1070, 1020, and 995 cm^{-1} are due to the asymmetric stretching of the P-O bonds. The band at 954 cm^{-1} is assigned to symmetric stretch-

ing vibrations of the P–O bond, while four bands at 627, 575, 560, and 538 cm^{-1} are attributed to asymmetric bending modes. In addition, the Raman spectra of all samples show the complementary bands at 396, 412, 465, 537, 570, 588, 619, 639, 967, 990, 1024, 1054, and 1071 cm^{-1} . The principal sharp band at 967 cm^{-1} is assigned to the symmetric stretching and those at 990 and 1024 cm^{-1} correspond to the asymmetric stretching of the PO_4 group. The bands at 1054 and 1071 cm^{-1} are from the splitting of the asymmetric stretching mode and those from 396 to 639 cm^{-1} are attributed to the deformation mode of the PO_4 group.¹⁴⁾ No clear differences are found between the spectra of the Ca- or Sr-doped LaPO_4 and CePO_4 pigments.

From the FT-IR and Raman results, the origin of the color change could be discussed from the change of 4f–5d transition energy by the solution of alkaline earth ions into the CePO_4 lattice accompanying the formation of oxide anion defects. In contrast to LaPO_4 , the reflectance spectrum of CePO_4 exhibits a strong absorption band in the UV region due to the optically allowed 4f–5d transition of cerium (Figs. 3 and 5), because Ce^{3+} has one 4f electron but there is no 4f electron in La^{3+} .¹⁵⁾ The 4f–5d transition is easily affected because 5d orbitals are exposed to significant interaction with orbitals of surrounding atoms and ions in cerium orthophosphate. For example, strong absorption based on 4f–5d transition has also been observed at around 450 nm in lithium cerium molybdate pigment to bring yellow hue.¹⁶⁾

In addition to the principal change of the 4f–5d transition discussed above, the partial production of Ce^{4+} is also suggested, because it has been reported that cerium is in the tetravalent form in double cerium phosphates of $\text{B}_{0.5}\text{Ce}_2(\text{PO}_4)_3$ (B = Mg, Ca, Sr, and Cd).¹⁷⁾ By the formation of tetravalent cerium ion, the O_{2p} – Ce_{4f} charge transfer transition also appears in the ultraviolet region and the Ce^{4+} produced affects the optical absorption of the 4f–5d transition. The 4f–5d transition correlates to the optical basicity which is modified by the partial oxidation of Ce^{3+} in the CePO_4 lattice, and the basicity increases after the oxidation of Ce^{3+} to Ce^{4+} to induce the red shift in the optical reflection spectrum.¹⁸⁾ Thus, the absorption around 610 nm could be attributed to an increase of basicity of the pigment.

Taking into account of the above results, the reason for the color change can be attributed to the existence of 4f electron in CePO_4 and combination of the main 4f–5d and the additional O_{2p} – Ce_{4f} charge transfer accompanying with the partial red shift of the former transition. Therefore, the remarkable color changes were observed in the CePO_4 solid solution pigments, while no color change appeared in the LaPO_4 -based pigments.

4. Conclusion

From the results discussed above, it can be concluded that the doping of divalent alkaline earth ions into the CePO_4 lattice induce not only the change of 4f–5d transition energy but also the partial oxidation of cerium ion. By combination of the principal 4f–5d transition of Ce^{3+} and the additional O_{2p} – Ce_{4f} transition of Ce^{4+} , the color of the cerium phosphate changes from white to yellow-green. In the case of LaPO_4 , on

the contrary, such effects are not observed because there is no 4f electron in this compound. More studies on possible applications of these powders as pigments in plastics and paints should be performed. However, the properties of the present Ca-, Sr-, or Ba-doped CePO_4 solid solutions suggest that this material has a potential to be applied as a satisfactory pigment for coating, because these pigments have advantages from the viewpoint of environmental pollution, compared with conventional toxic green pigments commercially applied.

Acknowledgements The authors sincerely thank Dr. Kuniaki Murase and Prof. Yasuhiro Awakura (Kyoto University) for their assistance with the Raman spectra measurements. The 21st COE Research Grant “Integrated EcoChemistry” supported this work for young researchers. This work was also partly supported by the Industrial Technology Research Grant Program in '02 (project ID: 02A27004c) 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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