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

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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 Ce3+ and the additional O3p–Ce4+ charge transfer transition of Ce4+ by the doping of alkaline earth ion into CePO4 lattice.

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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 (CePO4) 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 CePO4 based pigments have been characterized.

2. Experimental

The starting materials used for the synthesis of CePO4-based pigments were CePO4 (High Purity Chemicals, 99.9%), MgCO3 (Wako Chemicals, 99.99%), CaCO3 (Wako Chemicals, 99.99%), SrCO3 (Wako Chemicals, 99.99%), BaCO3 (Wako Chemicals, 99.9%), ZnCO3·H2O (Wako Chemicals, 97%), and (NH4)2HPO4 (Aldrich, 99.99%). These materials were thoroughly mixed in a molar ratio of CePO4 : MCO3 : (NH4)2HPO4 = 9 : 1 : 1 (M = Mg, Ca, Sr, Ba, 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 LaPO4 pigments were also synthesized as reference samples in the same procedure for the CePO4-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 Cu Kα 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 CePO4 pigments in comparison with that of pure CePO4. The single solid solution phase of
CePO₄ was obtained when Ca, Sr, or Ba was doped. The CePO₄ has a monazite-type monoclinic crystal structure⁷,⁸ 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 Ce³⁺ (0.120 nm for 9-coordinate⁹) is larger than that of Ca²⁺ (0.118 nm for 9-coordinate⁹) and is smaller than those of Sr²⁺ (0.131 nm for 9-coordinate⁹) and Ba²⁺ (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 Ce³⁺ 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 Mg₃P₂O₆ and Zn₃(PO₄)₂ were produced as the secondary phases, respectively.

The XRD patterns for the reference LaPO₄-based pigments are shown in Fig. 2 with that of pure LaPO₄. Similar results to the CePO₄ pigments were obtained, because the ionic radius of La³⁺ (0.122 nm for 9-coordinate⁹) is also larger than that of Ca²⁺ and is smaller than those of Sr²⁺ and Ba²⁺.

The color drastically changed from white to yellow-green by forming the solid solutions of Ca-, Sr-, and Ba-doped CePO₄. The effect of alkaline earth doping on the color of the CePO₄ 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 CePO₄. However, the reflectance spectra of the Ca-, Sr-, Ba-doped CePO₄ shows a strong absorption band under 500 nm and a relatively small and broad peak at 600–650 nm, compared with that of pure CePO₄. These peaks imply some variation of the crystal field strength by the solution of alkaline metal ions into the CePO₄ lattice. The change of the relative reflection intensities is responsible for the color change.

The L⁹a⁹b⁹ color coordinate data of pure CePO₄ and the Mg-, Ca-, Sr, Ba-, and Zn-doped CePO₄ pigments are summarized in Table 1. In this system, the L⁹ values are indicative of color lightness, while a⁹ and b⁹ 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure CePO$_4$</td>
<td>96.5</td>
<td>-0.54</td>
<td>+1.25</td>
<td>white</td>
</tr>
<tr>
<td>Mg-doped CePO$_4$</td>
<td>96.0</td>
<td>-0.54</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>Ca-doped CePO$_4$</td>
<td>73.2</td>
<td>-0.85</td>
<td>+13.2</td>
<td>yellow-green</td>
</tr>
<tr>
<td>Sr-doped CePO$_4$</td>
<td>73.4</td>
<td>-0.81</td>
<td>+15.9</td>
<td>yellow-green</td>
</tr>
<tr>
<td>Ba-doped CePO$_4$</td>
<td>75.1</td>
<td>-0.70</td>
<td>+14.4</td>
<td>yellow-green</td>
</tr>
<tr>
<td>Zn-doped CePO$_4$</td>
<td>77.2</td>
<td>-0.53</td>
<td>+16.2</td>
<td>white</td>
</tr>
<tr>
<td>Pure LaPO$_4$</td>
<td>90.0</td>
<td>-0.02</td>
<td>-10.6</td>
<td>white</td>
</tr>
<tr>
<td>Ca-doped LaPO$_4$</td>
<td>92.4</td>
<td>-0.47</td>
<td>14.1</td>
<td>white</td>
</tr>
<tr>
<td>Sr-doped LaPO$_4$</td>
<td>91.5</td>
<td>-0.20</td>
<td>+0.66</td>
<td>white</td>
</tr>
<tr>
<td>Ba-doped LaPO$_4$</td>
<td>90.1</td>
<td>-0.34</td>
<td>+0.92</td>
<td>white</td>
</tr>
</tbody>
</table>

$L^*$ 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. 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 4(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 blue) 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 orthophosphates. 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 molybdinate 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 Ba\(_2\)Ce\(_2\) (PO\(_4\))\(_3\) (B=Mg, Ca, Sr, and Cd).\(^{17}\) By the formation of tetravalent cerium ion, the O\(_{2g}\)–Ce\(_{4d}\) 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\(_{2g}\)–Ce\(_{4d}\) 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 the LaPO\(_4\)-based pigments.

4. Conclusion

From the results discussed above, it can be concluded that the doping of divergent 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\(_{2g}\)–Ce\(_{4d}\) 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.

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