Synthesis of an Environmentally Friendly and Nontoxic New Pigment Based on Rare Earth Phosphate

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A new inorganic pigment based on rare earth phosphate has been synthesized with the goal of preparing ecologically and environmentally friendly specific pigments. A yellow–green pigment that consists of nontoxic elements was obtained by doping calcium ions into the cerium orthophosphate lattice. Characterizations using XRD, UV–vis spectroscopy, and colorimetric assessment revealed that the formation of a Ca-doped $CePO_4$ solid solution was responsible for the appearance of the color.

Recently, discovery and development of new and improved inorganic pigments have been desired, because national laws and regulations in the ecological and toxicological area give pressures to replace well-known inorganic pigments containing toxic elements (e.g. Cd, Co, Cr, Hg, Pb, Sb, Se) with more environmentally friendly pigments or less toxic substances.[1] However, very few new inorganic pigments have been developed in recent decades. The use of high-performance organics is one way to get several colors, but these pigments have some limitations because of thermal and ultraviolet (UV)-ray radiation instabilities.

In this study, a new green pigment based on rare earth phosphate has been synthesized. In the synthesis, the starting materials containing nontoxic elements were employed and the pigments could be obtained only calcination in air by a simple solid-state reaction method. Rare earth phosphate is well-known material that exists in nature as a mineral (Monazite) and very stable against heat and UV-rays. In addition, metal phosphate is a main component of bone and tooth and, therefore, it is inert and safe not to give side effects to the human body.

Starting materials of $CePO_4$ (Purity: 99.9%) and $CaHPO_4 \cdot 2H_2O$ (Purity: 99.0%) were thoroughly mixed in a molar ratio of 3:2 in a mortar with a pestle. The mixture was calcined at 900 °C for 12 h in air. The obtained powder was characterized by means of X-ray powder diffraction (XRD, 40 kV and 50 mA, CuKα radiation, Rigaku Multiflex). Optical reflectance of the powder was measured with a UV-vis spectrometer (Shimadzu, UV-2450) using barium sulfate as a reference. Color of the sample was measured with a colorimeter (Minolta, CR-300) in the $L^*a^*b^*$ color spaces.

Figure 1 presents the X-ray powder diffraction result of the Ca-doped $CePO_4$ sample compared with that of pure $CePO_4$. The $CePO_4$ has a monazite-type monoclinic crystal structure[2,3] and the pattern shifted to higher angle by the calcium doping without any phase decompositions. Because the ionic radius of Ce^{3+} (0.120 nm for 9-coordinate[4]) is larger than that of Ca^{2+} (0.118 nm for 9-coordinate[4]), the X-ray result explicitly means that Ca-doped $CePO_4$ solid solution was successfully obtained as a single phase by the replacement of the Ce^{3+} site for Ca^{2+}.

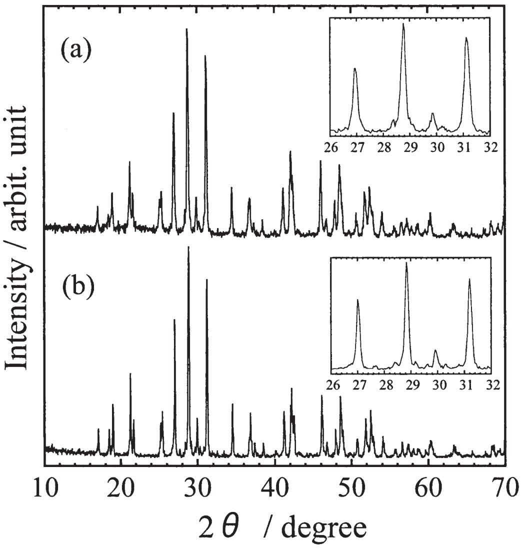

Figure 1. XRD patterns of (a) pure $CePO_4$ and (b) Ca-doped $CePO_4$ samples.

By forming the Ca-doped $CePO_4$ solid solution, the color drastically changed from white to yellow–green. The optical reflectance spectrum of the Ca-doped $CePO_4$ (Figure 2) shows a

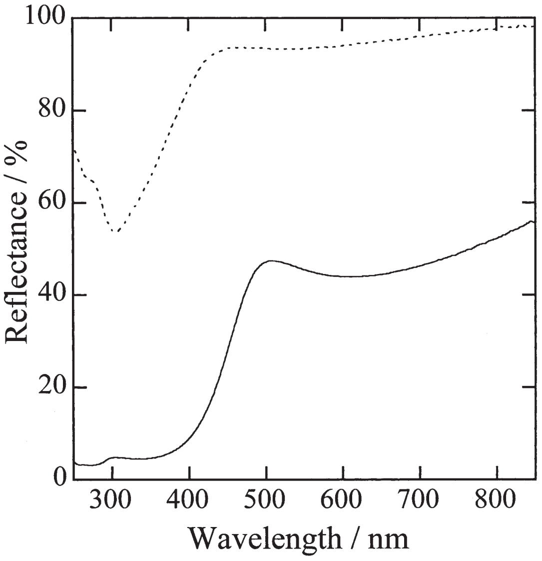

Figure 2. Reflectance spectra of pure $CePO_4$ (dotted line) and Ca-doped $CePO_4$ solid solution (solid line).

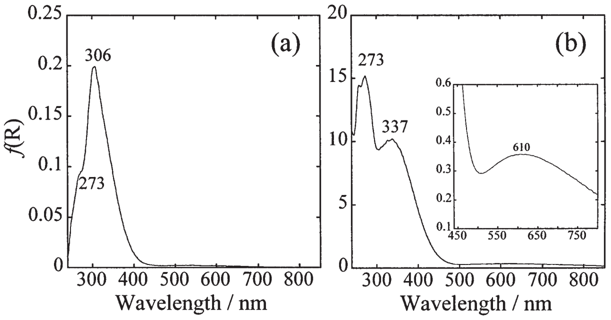

Figure 3. Absorbance of (a) pure $CePO_4$ and (b) Ca-doped $CePO_4$ solid solution.

strong absorption band under 500 nm and a relatively small and broad peak at around 600 nm, compared with that of pure $CePO_4$. These peaks imply some variation of the crystal field strength by the Ca doping. The change of the relative reflection intensities is responsible for the color coordinates variation.

The absorbance spectra of pure $CePO_4$ and Ca-doped $CePO_4$ represented with the remission function, $f(R) = (1 - R)^2/2R$, are depicted in Figure 3, where R is reflectance.[5,6] The weak absorption peaks were observed at 273 and 306 nm in pure $CePO_4$ (Figure 3a). By the calcium doping, the intensity of the peaks enhanced and the peak at 306 nm shifted to longer wavelength (337 nm) with tailing its edge to 450 nm. In addition, a new broad absorption peak appeared at 610 nm (the inset in Figure 3b). Absorptions of the visible light at around 400-450 (purple and blue) and 610 nm (red) correspond to the appearance of yellow and green colors, respectively, because yellow is complementary color to blue and green is the one to red.

Although the details of the mechanism of the color appearance have not been clear yet, it can be considered that the doping of divalent calcium ions into the trivalent cerium ion sites produced oxide defects in the $CePO_4$ lattice and the defect formation contributes to the change of band structure, which is correlated with the lattice deformation. Similar results reported in cerium phosphate glasses support this consideration because the band tailing started at lower energies when the disorder in the sample increased.[7]

The $L^*a^*b^*$ values of pure $CePO_4$ and the Ca-doped $CePO_4$ pigment 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, by the Ca doping, L^* and a^* decreased but b^* increased, indicating that the Ca-doped $CePO_4$ pigment has medium color lightness with the enhancement of green and yellow color. These results correspond to the above optical absorbance results.

Table 1. Actual color and coordinates in $L^*a^*b^*$ space of the pigments

Sample	L*	a*	b*	Color
pure $CePO_4$	96.0	+0.26	+1.69	white
Ca-doped $CePO_4$	68.0	−8.37	+15.4	yellow-green

Studies on more detail mechanism of the color appearance using band calculations and on possible applications of these powders as pigments in plastics and paints have not been performed yet. However, the properties of the Ca-doped $CePO_4$ suggests that this material has a potential to be applied as a satisfactory pigment for coating or coloring except for glaze which may cause a side reaction at high temperatures, especially taking into consideration the economics and ecologies in comparison with the relatively high price and toxic green chromium oxide pigments commercially applied.

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