Preparation and Characterization of Amorphous $Ce_{1-x}Zr_xW_2O_8$ Fine Particles for Environmental-friendly Yellow Pigments

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New inorganic pigments based on amorphous cerium tungstate have been synthesized with the goal of preparing ecologically and environmental-friendly specific pigments. These pigments consist of all non-toxic elements and show brilliant yellow color. The reason for the color change was attributed to the modification of the O_{2p}–Ce_{4f} and the O_{2p}–W_{5d} double charge transfer transitions with the Zr doping.

Recently, development of new colored inorganic pigments has been desired to substitute for the conventional pigments containing toxic elements (Cd, Co, Cr, Hg, Pb, Sb, and Se) which are hazardous to health and the environment.[1] Although the use of high-performance organic pigments is an alternative way to give several colors, thermal and UV (ultraviolet ray) stabilities are not satisfactory.

As new yellow pigments without toxic metals to substitute for the conventional CdS, $PbCrO_4$, and $PbMoO_4$, cerium thiosilicates[2] and the perovskites $CaTaO_2N$ and $LaTaON_2$[3] have been proposed. However, there are still some problems in their synthesis processes. The heating condition must be controlled exactly to synthesize the cerium thiosilicates and this method is too time-consuming process (at least 13 days). In the case for the perovskites, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long period (20–60 h) to synthesize them. Although some alternative yellow pigments based on cerium oxide have also been reported, but their chromatic properties are not satisfactory for industrial use.[4,5]

In the present study, new yellow pigments based on amorphous cerium tungstate, $Ce_{1-x}Zr_xW_2O_8$ ($0 \leq x \leq 0.6$), were synthesized and their color properties were characterized from the viewpoint of possible ecological inorganic pigments. According to the phase diagram for the cerium tungstate,[6] cerium ion usually exists in trivalent state in the crystalline tungstates and successful synthesis of CeW_2O_8 is generally restricted in the crystalline form. However, it becomes possible to prepare the CeW_2O_8 phase in the amorphous state.[7] Furthermore, double charge transfer of O_{2p}–Ce_{4f} and O_{2p}–W_{5d} usually brings about brilliant yellow hue, when both Ce^{4+} and W^{6+} coexist in the amorphous state. These pigments presented in this study can be prepared in a short period by a simple coprecipitation method in an atmospheric air. Furthermore, the new pigments can be inherently safe substitutes even if they are entered into the environment in a bioavailable form through waste-disposal sites and incineration plants, because they are composed of non-toxic elements.

The $Ce_{1-x}Zr_xW_2O_8$ ($0 \leq x \leq 0.6$) particles were synthesized by the coprecipitation method. Cerium(IV) sulfate tetrahydrate and zirconium oxynitrate dihydrate were dissolved into a 1 mol·dm^{-3} sulfuric acid solution in a stoichiometric ratio, adjusting the total concentration of the cations to be 0.2 mol·dm^{-3}. The mixed solution was added to a 0.2 mol·dm^{-3} sodium tungstate aqueous solution and then a 1 mol·dm^{-3} sulfuric acid solution was dropped into the solution to adjust the pH value to be 2.2 in order to promote the precipitation effectively.[8] After aging overnight at room temperature, the precipitate was separated by centrifuging. The powder obtained was washed with deionized water for five times, and dried in an oven at 353 K for 24 h.

The pigments prepared were characterized by means of X-ray powder diffraction (XRD, 40 kV and 50 mA, Cu Kα, Rigaku Multiflex). The compositions of the samples were confirmed using an X-ray fluorescence spectrometer (Rigaku ZEX-100e) and a TG-DTA analyzer (Shimadzu DTG-50). Optical reflectance of the powder was measured with a UV–vis spectrometer (Shimadzu UV-2450) using barium sulfate as a reference. 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 brightness 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).

All samples were confirmed to be amorphous from the X-ray powder diffraction patterns, and the chemical composition was $Ce_{1-x}Zr_xW_2O_8 \cdot 2.0H_2O$ ($0 \leq x \leq 0.6$). Figure 1 shows the absorbance spectra represented with the Kubelka–Munk absorp-

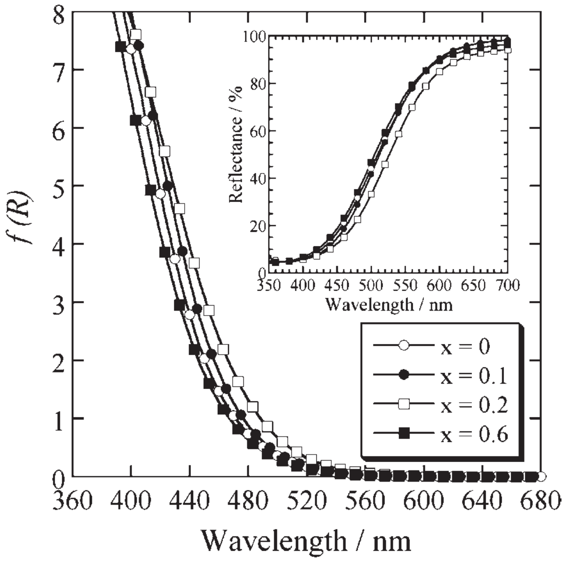

Figure 1. Absorbance spectra of the amorphous $Ce_{1-x}Zr_x$-W_2O_8 pigments.

Table 1. Optical gap energy and $L^*a^*b^*$ color coordination of the amorphous $Ce_{1-x}Zr_xW_2O_8$ pigments

x in $Ce_{1-x}Zr_xW_2O_8$	E_g/eV	L^*	a^*	b^*
0	2.67	86.9	0.98	58.5
0.1	2.64	87.1	0.61	62.4
0.2	2.55	83.6	4.19	68.2
0.4	2.66	88.2	−1.09	59.8
0.6	2.70	87.4	−1.34	56.0

tion function, $f(R) = (1 - R)^2/2R$, where R is reflectance[9] and the corresponding reflectance spectra are also depicted in the inset. The strong optical absorption behavior was observed in all samples under 520 nm, which corresponds to the blue region. As a result, the color of the samples becomes yellow because blue is a complementary color to yellow. The absorption wavelength depends on the amount of zirconium, and the maximum absorption in longer wavelengths was observed at the composition of $Ce_{0.8}Zr_{0.2}W_2O_8$ in comparison with the other samples.

The optical gap energies (E_g) of the $Ce_{1-x}Zr_xW_2O_8$ samples determined from the absorbance spectra are tabulated in Table 1. The optical gap energy strongly depends on the composition, and takes the lowest value for $Ce_{0.8}Zr_{0.2}W_2O_8$ (2.55 eV), which corresponds to the result of the absorption spectrum described above.

The $L^*a^*b^*$ color coordinate data of the $Ce_{1-x}Zr_xW_2O_8$ pigments are also summarized in Table 1. In this system, an ideal yellow pigment will show that $(L^*a^*b^*) = (100\ 0\ 100)$. The color of the pigments was brilliant yellow, but the hue depends on the zirconium content in the samples, accompanying with the change of the optical energy gap. The color modifications are related to the amount of Zr incorporated into the amorphous CeW_2O_8. The specific a^* value of the $Ce_{0.8}Zr_{0.2}W_2O_8$ pigment is due to higher optical absorption in the green range from 480 to 560 nm than the others as depicted in Figure 1. The $Ce_{0.8}Zr_{0.2}W_2O_8$ pigment (Figure 2) was most yellowish from the value of b^* which is correlated with the yellow element.

Although the details of the mechanism of the color change with the variation of the chemical composition have not been clear yet, the observed shift of the gap energy must be attributed to the changes of the width or the position of the conduction bands for different chemical compositions. In amorphous CeW_2O_8, the optical absorption is caused by the multiple effects of the O_{2p}–Ce_{4f} and the O_{2p}–W_{5d} charge transfer transitions. The optical absorption is usually observed around 400 and 450 nm for the former and the latter, corresponding to the bandgap energies of CeO_2 (3.10 eV)[10] and WO_3 (2.77 eV), respectively.[11]

Incorporation of zirconium in the amorphous CeW_2O_8 will cause the disordering in the pigment and may be one of the reasons behind the changing of the optical gap, leading to the change of the hue. Since the atomic weight of zirconium (91.22) is smaller than that of cerium (140.1), the increase in the Zr doping in the amorphous CeW_2O_8 causes the decrease in the density of the pigment particle. According to a reference, bandgap energy decreases as the material becomes less dense,[12] and, therefore, the optical energy gap in the present pigment decreases with the Zr addition, leading to the enhancement of yellow color. However, the contribution of the O_{2p}–Ce_{4f} transfer becomes small when an excess amount of Zr is doped into the pigment, because the amount of cerium decreases inversely proportional to the zirconium addition. As a result, the optimum composition to give the most yellowish hue exists in the amorphous $Ce_{1-x}Zr_xW_2O_8$ samples, that is, $Ce_{0.8}Zr_{0.2}W_2O_8$. These pigments take full advantage of the amorphous state to show the effective hue, and thus the feature characteristics deteriorate when they crystallize.

Figure 2. A representative photograph of the amorphous $Ce_{0.8}Zr_{0.2}W_2O_8$ pigment.

In summary, new inorganic pigments based on amorphous $Ce_{1-x}Zr_xW_2O_8$ have been synthesized. The optical absorption energy of these pigments depends on the Zr content, and the most effective hue can be obtained at $x = 0.2$. The properties of the present pigments suggest that these materials have a potential to be new environmental-friendly pigments, because they are composed of all non-toxic elements.

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