Synthesis and Characterization of CeO_2–ZrO_2–Bi_2O_3 Solid Solutions for Environment-friendly Yellow Pigments

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CeO_2–ZrO_2–Bi_2O_3 solid solutions have been synthesized by a citrate complex route. The resulting colored materials have been characterized as potential environment-friendly pigments. The yellow hue of the pigment was significantly enhanced by the introduction of zirconium and bismuth into the CeO_2 lattice, which produces intrinsic strain and a hybrid orbital of Bi_{6s} and O_{2p}, respectively. The yellow pigments obtained have been found to be effective alternatives to the conventional toxic colored materials.

The use of nontoxic raw materials in the chemical industries is becoming important to prevent health hazards and environmental damage.[1] In the field of pigments, it has been necessary to develop environment-friendly materials to substitute for the conventional pigments containing toxic elements (e.g., Cd, Co, Cr, Hg, Pb, Sb, and Se). However, only a limited number of nontoxic pigments can satisfy requirements of high thermal and chemical stabilities particularly in the case of yellow pigments.[2–6]

Among the several candidates for the alternative nontoxic yellow pigments, CeO_2 and its related materials have been attracted because of the opacity, low toxicity, and high-temperature stability.[6,7] The coloring mechanism is based on the charge-transfer band from O_{2p} to Ce_{4f} in the semiconducting CeO_2. The band gap between the anionic O_{2p} valence band and the cationic Ce_{4f} conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence band and the conduction band. As a result, shift of the charge-transfer band is observed.

In this work, new pigments based on ternary CeO_2–ZrO_2–Bi_2O_3 solid solutions have been synthesized. Although these materials were studied in details in our laboratory as oxygen-storage materials for automotive exhaust catalysts,[8] their color properties have not been characterized. Here, we have characterized the color properties from the viewpoint of possible ecological inorganic yellow pigments. Doping of Zr^{4+} into the CeO_2 lattice produces intrinsic strain, which will affect the O_{2p} valence band. Furthermore, coexistence of Bi^{3+} in the CeO_2–ZrO_2 lattice will enhance the visible light absorption by the formation of a hybrid orbital of Bi_{6s} and O_{2p}. The inorganic yellow pigments presented in this study can be synthesized by a simple citrate complex method in an atmospheric air, using nontoxic elements. It is expected, therefore, that the pigments can be inherently safe in a workplace and waste-disposal sites and will give no environmental deterioration.

In our previous study on the catalysis of the $Ce_xZr_{1-x}O_2$ solid solutions, we found that those close to $x = 0.55$ compatible with a cubic symmetry showed the deepest yellow hue as well as high redox activity due to the distortion of oxide anions in the bulk of the solid solution.[9] Accordingly, in the preparation of the CeO_2–ZrO_2–Bi_2O_3 pigments, the Ce:Zr ratio was fixed to 55:45 and the molar ratio of bismuth has been adjusted from 5 to 25 mol % at intervals of 5 mol %.

The CeO_2–ZrO_2–Bi_2O_3 solid solutions were synthesized from nitrate precursors by complexing the cations with the citrate. After mixing the aqueous solutions of 1.0 mol·dm^{-3} $Ce(NO_3)_3$, 1.0 mol·dm^{-3} $ZrO(NO_3)_2$, and 0.5 mol·dm^{-3} $Bi(NO_3)_3$, adjusting the total amount of the cations to be 20 mmol, an aqueous solution of 1.0 mol·dm^{-3} citric acid (30 dm^3) was added. The resulting solution was stirred at 353 K for 5 h. A solid obtained was dried at 403 K and then heated at 573 K for 1 h and successively at 1273 K for 1 h to obtain a yellow powder. The compositions of the pigments analyzed by an X-ray fluorescence spectrometer (Rigaku ZEX-100e) are summarized in Table 1.

X-ray powder diffraction (XRD) patterns of the pigments were collected (Rigaku Multiflex, 40 kV and 50 mA, Ni-filtered Cu Kα). Optical reflectance spectra were obtained with a UV–vis spectrometer (Shimadzu UV-2450) using barium sulfate as a reference. Color properties were evaluated in terms of CIE $L^*a^*b^*$ system with a chroma meter (Minolta, CR-300). The value L^* represents the brightness or darkness of the color as related to a neutral grey scale. The values a^* (the axis red-green) and b^* (the axis yellow-blue) indicate the color hue. The BET specific surface area was measured using nitrogen adsorption (Mircometrics FlowSorb II 2300).

Figure 1 shows the X-ray powder diffraction results of the CeO_2–ZrO_2–Bi_2O_3 samples. A single phase of cubic fluorite structure was obtained for the pigments in which the bismuth content was 20 mol % or less, while in the sample that the Bi^{3+} content was 23 mol %, Bi_2O_3 was observed as a secondary phase. In the region forming the single fluorite phase, the XRD pattern shifted to higher angles with the increase in the Bi content. This result shows that solid solutions were successfully obtained. Although the ionic radius of Bi^{3+} (0.117 nm) is larger than those of Ce^{4+} (0.097 nm) and Zr^{4+} (0.084 nm) in eight coordination,[10] the diffraction pattern of the CZB component shifted to higher angles because of the formation of oxide anion vacancies.

The effects of increasing Bi content on the color of the pig-

Table 1. Composition of the CeO_2–ZrO_2–Bi_2O_3 pigments

Sample composition	Ce:Zr	Bi content/mol %
$Ce_{0.56}Zr_{0.44}O_{2.0}$	56:44	0
$Ce_{0.53}Zr_{0.42}Bi_{0.05}O_{1.975}$	56:44	5
$Ce_{0.50}Zr_{0.40}Bi_{0.10}O_{1.95}$	56:44	10
$Ce_{0.47}Zr_{0.38}Bi_{0.15}O_{1.925}$	55:45	15
$Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$	54:46	20
$Ce_{0.42}Zr_{0.35}Bi_{0.23}O_{1.89}$	55:45	23

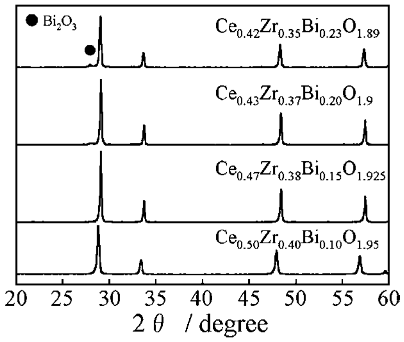

Figure 1. X-ray powder diffraction patterns of the CeO_2–ZrO_2–Bi_2O_3 pigments.

Table 2. $L^*a^*b^*$ color coordinate, optical energy gap (E_g), and BET specific surface area (S.A.) of the CeO_2–ZrO_2–Bi_2O_3 pigments

Pigment	L^*	a^*	b^*	E_g/eV	S.A./$m^2 \cdot g^{-1}$
$Ce_{0.56}Zr_{0.44}O_{2.0}$	96.9	−3.66	14.3	3.26	6.8
$Ce_{0.53}Zr_{0.42}Bi_{0.05}O_{1.975}$	92.9	−6.65	43.5	2.73	4.0
$Ce_{0.50}Zr_{0.40}Bi_{0.10}O_{1.95}$	88.4	−2.15	56.3	2.64	2.2
$Ce_{0.47}Zr_{0.38}Bi_{0.15}O_{1.925}$	86.9	1.76	63.0	2.59	0.8
$Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$	83.0	6.93	68.9	2.54	0.9
$Ce_{0.42}Zr_{0.35}Bi_{0.23}O_{1.89}$	78.1	12.5	65.0	2.43	0.7

ment powders were summarized in Table 2. The optical energy gaps (E_g) of the CeO_2–ZrO_2–Bi_2O_3 samples determined from the reflectance spectra and the BET specific surface area are also tabulated. When the bismuth content increases, there is only a slight increase in the red component (a^*), while the yellow component (b^*) increases drastically giving rise to progressive brilliant hue of the samples. The most attractive yellow color was obtained for $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$. However, in the $Ce_{0.42}Zr_{0.35}Bi_{0.23}O_{1.89}$ sample, the yellow hue faded owing to the secondary phase formation.

Figure 2 depicts the diffuse reflectance spectra obtained for the CeO_2–ZrO_2–Bi_2O_3 solid solutions. The strong optical absorption behavior was observed in all samples in the region of shorter wavelength than 500 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 position of the reflectance edge depends critically on the bismuth content, and the maximum absorption in longer wavelengths was observed at the composition of $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$ in comparison with the other samples, which corresponds to the color coordinates in Table 2.

In CeO_2–ZrO_2, the 4f valence cell of Ce^{4+} is empty and that of O^{2-} is fully occupied. The 4f orbitals overlap in a cationic conduction band and overlap of oxide anions gives to an anionic valence band. The optical absorption of CeO_2–ZrO_2 is due to the charge-transfer transition between cerium and oxygen. In the CeO_2–ZrO_2–Bi_2O_3 pigments, on the contrary, the 6s electrons of the bismuth valence shell introduces an additional electronic level of energy between the O^{2-} valence band and Ce^{4+} conduction band, and reduced band gap energies are observed. According to a reference on $BiVO_4$,[11] it is suggested that the valence bands are made up by a hybrid orbital of Bi_{6s} and O_{2p} and the visible light absorption corresponds to the transition from the hybrid orbital to the conduction band. As a result, the CeO_2–ZrO_2–Bi_2O_3 pigments absorb in the wavelength region below 500 nm with the decrease in the band gap energies, producing a yellow color.

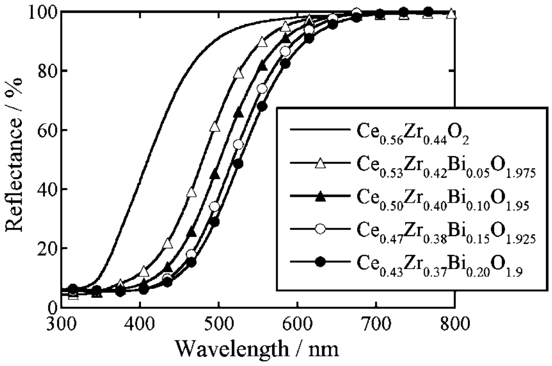

Figure 2. Diffuse reflectance spectra obtained for various compositions of the CeO_2–ZrO_2–Bi_2O_3 solid solutions.

In conclusion, new inorganic yellow pigments, CeO_2–ZrO_2–Bi_2O_3 solid solutions, were successfully synthesized. It is suggested that the coloring mechanism is based on the modification of the valence band by forming a hybrid orbital of Bi_{6s} and O_{2p}. The CeO_2–ZrO_2–Bi_2O_3 solid solutions have high thermal stability and are composed of all nontoxic elements. Therefore, they are expected to be new environment-friendly pigments.

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