Novel Nontoxic and Environment-friendly Inorganic Yellow Pigments

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Synthesis and characterization of novel and environment-friendly inorganic yellow pigments were successfully realized. The pigments are composed of CeO_2, Bi_2O_3, and SiO_2, which are nontoxic materials with the potential to give brilliant color. These new materials have high thermal and UV stability; thus, they are ideal candidates for use as environment-friendly inorganic yellow pigments.

The application of nontoxic materials in the chemical industry has become a significant area of interest, with the aim of reducing health hazards and environmental damage. However, several popular pigments are based mainly on toxic transition metal or heavy metal ions. In particular, the most popular inorganic yellow pigments for plastics and paints for traffic markings are CdS (cadmium yellow) and $PbCrO_4$ (chrome yellow), respectively. For this reason, there have long been efforts to develop environment-friendly yellow pigments that can substitute for the conventional ones containing toxic elements. We demonstrate here the synthesis and characterization of environment-friendly inorganic yellow pigments composed of CeO_2, Bi_2O_3, and SiO_2, which are nontoxic materials with the potential to give brilliant color.

The brilliant colors of inorganic pigments are usually due to selective absorption of visible light. The electronic transition between the valence band and conduction band in semiconductor solids in the visible spectrum results in pure and brilliant color. The width (energy) of the optical band gap depends on both the extent of overlap of the valence orbitals and the difference in electronegativity between the cations and anions involved in the transition. Modification of the band structure allows artificial control of the band gap width to produce new inorganic pigments.

Doping a host lattice with a metal ion, which can preferentially affect a continuous valence band by forming a hybrid orbital with the O 2p orbital, is effective in conferring the material with an absorption edge in the visible light region. This strategy has been utilized in the field of visible-light photocatalysts in order to shrink the band gap energy of semiconductors.[1] Among several candidate transition metal and main group metal ions, including Bi^{3+}, Sn^{2+}, and Ag^{+}, we chose Bi^{3+} because inorganic salts and oxides of this element have been confirmed as virtually nontoxic in medical references.[2]

The concept described above can be combined with the use of rare earth refractory oxides. Rare earth elements generally have a low toxicity rating; in particular, cerium oxide has been tested for acute effects and was found to have low toxicity.[3] In the course of a systematic search of CeO_2-based pigments containing bismuth, $(Bi_{1-x}Ce_x)_2O_3$ materials were synthesized and characterized,[4] but the color of the resulting material was pale yellow. We previously reported that incorporation of the Zr^{4+} ion, whose ionic radius is smaller than Ce^{4+} and Bi^{3+}, into the Bi_2O_3–CeO_2 lattice was effective in enhancing the yellow hue.[5] However, the resulting color was still unsatisfactory.

In order to search for an idea that might lead to a breakthrough, we focused on one element, silicon. Silicon is nontoxic in its elemental form and in all naturally occurring forms, namely silica and silicates. We previously reported that the band gap energy of CeO_2 could be reduced by addition of SiO_2.[6] This led us to expect that CeO_2–SiO_2–Bi_2O_3 materials would be promising candidates for new inorganic yellow pigments. We, therefore, synthesized several samples to verify our concept of band gap control as a rational tool for the design of yellow pigments.

In our previous study on $(1-x)SiO_2$–$xCeO_2$,[6] we found that the sample around $x = 0.5$ showed relatively deeper yellow color than the others. Accordingly, the Ce:Si ratio was fixed to 1:1 in this study. The $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ pigments studied here were synthesized by a sol–gel method. After mixing tetraethoxysilane (TEOS) and aqueous solutions of $1.0\,mol\,dm^{-3}$ $Ce(NO_3)_3$ and $0.5\,mol\,dm^{-3}$ $Bi(NO_3)_3$, adjusting the total amount of the cations (Si, Ce, and Bi) to 20 mmol, an aqueous solution of $3\,mol\,dm^{-3}$ HNO_3 ($20\,cm^3$) was added, and the mixture was stirred at room temperature for 5 h. With the pH value of the solution maintained at 10, the mixture was then stirred for a further 3 days. Next, the solvent was evaporated at 423 K using a rotary evaporator, and a solid obtained was heated at 1023 K for 1 h. Before characterization, the samples were gently ground in an agate mortar.

The pigments were characterized by X-ray powder diffraction (XRD, Rigaku Multiflex). A single-phase cubic fluorite structure with low crystallinity was observed for the $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ pigments in which the bismuth content was 33 mol % or less, and there were no extra lines due to other compounds or mixed phases, while in a sample with a Bi^{3+} content of 44 mol %, $Bi_4(SiO_4)_3$ was observed as a secondary phase (see Supporting Information).[10]

Optical reflectance was measured with a UV–vis spectrometer (Shimadzu UV-2550) using barium sulphate as a reference. The UV–vis reflectance spectra are shown in Figure 1. The positions of the absorption edges for $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ depend on the composition, and the edge energy varies from 2.90 to 2.37 eV. Thus, it appears that the yellow color can be varied by appropriate adjustment of the x and y values. The color coordination values and the edge energies of $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$, and, for comparison, those of the commercial pigment praseodymium yellow, are given in Table 1. The $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ pigments fully correspond to the pale- to deep-yellow color range. As the bismuth content increases, there is only a slight increase in the red component (a^*), while the yellow component (b^*) increases sharply, giving rise to the progressively brilliant hues of the samples (see Supporting Information for details of these color description systems).[10] In the sample with a Bi^{3+} content of 44 mol %, however, the yellow color faded a little, be-

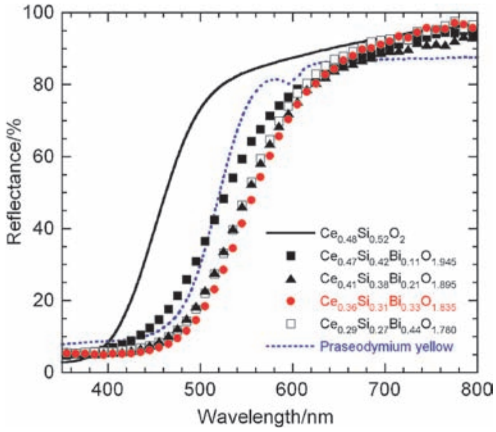

Figure 1. UV–vis diffuse reflectance spectra obtained for $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ pigments of various compositions.

Table 1. Color and edge energy data (E_g) of $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$ and commercial praseodymium yellow

Sample	L^*	a^*	b^*	E_g/eV
$Ce_{0.48}Si_{0.52}O_{2.0}$	91.6	−6.60	29.2	2.90
$Ce_{0.47}Si_{0.42}Bi_{0.11}O_{1.945}$	80.7	2.27	59.0	2.51
$Ce_{0.41}Si_{0.38}Bi_{0.21}O_{1.895}$	77.9	10.9	70.5	2.40
$Ce_{0.36}Si_{0.31}Bi_{0.33}O_{1.835}$	74.3	15.6	72.7	2.37
$Ce_{0.29}Si_{0.27}Bi_{0.44}O_{1.780}$	76.3	13.1	68.0	2.40
Praseodymium yellow	83.5	−3.28	70.3	2.43

cause of the $Bi_4(SiO_4)_3$ impurity formation. The most attractive yellow hue was achieved using $Ce_{0.36}Si_{0.31}Bi_{0.33}O_{1.835}$ via optimization. In this case, the b^* value corresponding to the yellow component was greater than that exhibited by the commercial praseodymium yellow, in agreement with the reflectance spectra shown in Figure 1.

The thermal stability of these pigments in air (the onset of decomposition for $Ce_{0.36}Zr_{0.31}Bi_{0.33}O_{1.835}$ is at 1023 K) is far superior to those of the competing cadmium yellow (693 K) and $Ca_{1.95}La_{0.05}TaO_{2.95}N_{1.05}$ (693 K).[7] Furthermore, no change in color was observed after an accelerated weathering test consisting of continuous exposure under a UV-A lamp (peak wavelength 352 nm) in air at ambient temperature.

The satisfactory results obtained in these tests can be ascribed to the chemical and physical properties of oxide-based materials. In CeO_2, the 4f valence shell of Ce^{4+} is empty, while that of O^{2-} is fully occupied. The 4f orbitals overlap in a cationic conduction band, while overlap of the 2p orbitals of the oxide anions gives rise to an anionic valence band. Accordingly, the optical absorption of CeO_2 is caused by the charge-transfer transition from O 2p to Ce 4f. Doping of Bi^{3+} ions into the CeO_2 lattice results in enhancement of visible light absorption due to the transition from a new valence band, made up of a hybrid orbital of Bi 6s and O 2p, to the Ce 4f conduction band,[1] and the presence of Si^{4+} in the CeO_2 lattice induces the formation of intermediate energy levels in the CeO_2 semiconductor on either side of Fermi level, resulting in a change in the band gap.[8] We can conclude, therefore, that the coloring of the materials is due to synergetic modification of the band structure by the hybrid orbital formed from the Bi 6s and O 2p orbitals, as well as the formation of intermediate energy levels due to Si^{4+} doping. In support of this, a similarly brilliant yellow hue was not observed for $Ce_{0.36}Si_{0.31}La_{0.33}O_{1.835}$, in which La^{3+} (ionic radius 0.116 nm for eight-coordination, 0.103 nm for six-coordination,[9] almost identical to that of Bi^{3+}) is included instead of Bi^{3+} at the same composition, or for CeO_2–Bi_2O_3[4] or CeO_2–SiO_2.[6]

Figure 2. Representative photograph of $Ce_{0.36}Si_{0.31}Bi_{0.33}O_{1.835}$.

We successfully demonstrated the synthesis of new inorganic yellow pigments with the formula $Ce_{1-x-y}Si_xBi_yO_{2-y/2}$. Figure 2 shows the photograph of the material with the composition $Ce_{0.36}Si_{0.31}Bi_{0.33}O_{1.835}$, demonstrating its warm and brilliant color, which makes it ideal for use as a pigment. These new materials are composed entirely of nontoxic elements, and have high thermal and UV stability; thus, they are ideal candidates for use as environment-friendly inorganic yellow pigments.

This work was supported by a Grant-in-Aid for Science Research (No. 19750171) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.