Synthesis and Characterization of Ca$_{1-x}$Eu$_x$ZrO$_3$ as Environmentally Friendly Inorganic Yellow Pigments

Kohei Minagawa, Yuichi Nishiguchi, Ryohei Oka, and Toshiyuki Masui*

ABSTRACT: Eu$^{2+}$-doped calcium zirconates, Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ x ≤ 1), were synthesized as novel environmentally friendly inorganic yellow pigments by the conventional solid-state reaction method. The crystal structure, morphology, optical properties, and color were characterized. The Eu$^{2+}$-doped samples strongly absorbed blue light in the wavelength range of 435–480 nm, which was caused by the 4f−5d allowed transition of Eu$^{2+}$. The color of the sample gradually became brilliant yellow with increasing the Eu$^{2+}$ content. Among the samples synthesized in this study, the brightest yellow color was obtained with the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ (a* = +11.5 and b* = +70.7) sample. Compared with the commercially available praseodymium yellow pigment (a* = −3.28, b* = +70.3), the yellowness value (b*) of Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ was comparable and the redness value (a*) was higher. As a result, this pigment exhibited a reddish yellow color as compared with praseodymium yellow. In addition, this pigment was chemically stable. Therefore, the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment has the potential to become a novel environmentally friendly inorganic yellow pigment.

1. INTRODUCTION

Inorganic pigments have a wide range of applications such as in ceramics, plastics, and glasses due to their high thermal stability and hiding power. In particular, yellow pigments have high visibility and are applied to paints for road markers and warning sign boards. However, several industrial yellow pigments such as cadmium yellow (CdS), chrome yellow (PbCrO$_4$), and nickel titanium yellow (TiO$_2$−NiO−Sb$_2$O$_3$) contain the harmful elements (e.g., Cd, Pb, Cr, and Sb) for the human body as well as the environment. Therefore, development of novel yellow pigments without toxic elements is required, and a number of studies have been reported by several researchers.1−9

Because of this situation, we focused on a divalent europium (Eu$^{2+}$) ion as a yellow coloring source. Eu$^{2+}$ has been generally used as an activator for phosphor materials.10−18 KBaGd$_2$Si$_2$O$_7$:Eu$^{2+}$, Sr$_5$MgLn(PO$_4$)$_3$:Eu$^{2+}$ (Ln = Y and La), and Li$_2$CaSiO$_4$:Eu$^{2+}$ as the examples of the Eu$^{2+}$-doped phosphors absorb the visible light in the wavelength range from 350 to 430 nm due to the electronic transition between 4f and 5d orbitals.16−18 The energy level of the 5d orbital of Eu$^{2+}$ is strongly affected by the surrounding crystal field. Accordingly, the absorption wavelength due to the 4f−5d allowed transition depends on the host crystal structure. In the case of phosphor, the concentration of Eu$^{2+}$ is controlled by about 1 mol % to prevent concentration quenching, and the optical absorption is weak because of the small Eu$^{2+}$ content. Therefore, it is considered that the coloration of the samples can be seen by further increasing the content of Eu$^{2+}$.

In this study, we selected perovskite-type calcium zirconate (CaZrO$_3$) as a host material for the environmentally friendly yellow pigment, which is composed of only nontoxic elements. In addition, CaZrO$_3$ has a high melting point ($T_m$ = 2365 °C) and sufficient chemical stability.19,20 Hence, this compound is well-known as a mother for rare-earth-doped phosphors, such as CaZrO$_3$:RE$^{3+}$ (RE$^{3+}$ = Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, and Tm$^{3+}$).21−23 When Eu$^{2+}$ is doped into the Ca$^{2+}$ site, the crystal field around the Eu$^{2+}$ ion should be strong because the ionic radius of Ca$^{2+}$ (0.112 nm for 8 coordination) is smaller than that of Eu$^{2+}$ (0.125 nm for 8 coordination).24 As a result, the crystal field splitting of the 5d orbitals of Eu$^{2+}$ becomes large, and the transition energy of Eu$^{2+}$ from the 4f to 5d orbitals is expected to be small, corresponding to the wavelength of visible light. That is, it is expected that a part of visible light will be absorbed, and the sample will be colored. Therefore, Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ x ≤ 1) pigments were synthesized by using a conventional solid-state reaction technique, and the optical and color properties were characterized.

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2. RESULTS AND DISCUSSION

2.1. X-Ray Powder Diffraction and Field-Emission-Type Scanning Electron Microscopic Image. Figure 1 shows the X-ray powder diffraction (XRD) patterns of the Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ $x$ ≤ 1) samples. Single-phase perovskite structures were obtained in the $x = 0$ and 0.1 samples. A small amount of ZrO$_2$ was detected as an impurity when $x$ was in the range 0.2 ≤ $x$ ≤ 0.4, but the samples were obtained in almost single phase. However, no perovskite-type structure was obtained with EuZrO$_3$ ($x = 1$), and only diffraction peaks attributed to the Eu$_2$Zr$_2$O$_7$ phase were observed.

CaZrO$_3$ has an orthorhombic perovskite structure with the symmetry of the $Pnma$ (no. 62) space group. In the CaZrO$_3$ structure, the coordination number (CN) values of Ca$^{2+}$ and Zr$^{4+}$ are 8 and 6, respectively. The lattice volumes of the Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ $x$ ≤ 0.4) samples were calculated from the diffraction peak angles. The composition dependence of the lattice volume of Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ $x$ ≤ 0.4) is shown in Figure 2. The lattice volume increased with increasing the Eu$^{2+}$ concentration. This indicates that Ca$^{2+}$ (ionic radius: 0.112 nm for CN = 8) ions were partially substituted with larger Eu$^{2+}$ (ionic radius: 0.125 nm for CN = 8) ions. The lattice volume of EuZrO$_3$ estimated using the fitted straight line in Figure 2 was 0.2785 nm$^3$, which was larger than that reported by Viallet et al. (0.2756 nm$^3$). This result suggests that some Eu$^{3+}$ ions were also introduced into the Zr$^{4+}$ site of Ca$_{1-x}$Eu$_x$ZrO$_3$, because the ionic radius of Eu$^{3+}$ (0.0947 nm for CN = 6) is larger than that of Zr$^{4+}$ (0.072 nm for CN = 6).

Figure 3 shows field-emission-type scanning electron microscopy (FE-SEM) images of Ca$_{1-x}$Eu$_x$ZrO$_3$ ($x = 0.1$, 0.2, 0.3, and 0.4) samples. Particles about 1.0 μm in size were observed in these samples, although they were partially fused since the calcination temperature was as high as 1400 °C.

2.2. X-Ray Photoelectron Spectra. The X-ray photoelectron spectra (XPS) of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ sample is shown in Figure 4. The spectrum in Figure 4a provided information on the chemical state of Eu$^{2+}$ and Eu$^{3+}$ in the near-surface region. The peaks at 1123.8 and 1154.0 eV were attributed to the Eu$^{2+}$ 3d$^{5/2}$ and 3d$^{3/2}$ configurations, while the strong peaks observed at 1133.8 and 1163.6 eV corresponded to the Eu$^{3+}$ 3d$^{5/2}$ and 3d$^{3/2}$ lines, respectively. These results indicated that Eu$^{2+}$ and Eu$^{3+}$ coexisted in the sample. The ratio of Eu$^{2+}$ to Eu$^{3+}$ was estimated to be 1:4 based on the deconvoluted peak area. Therefore, the dominant oxidation state of europium ions was trivalent on the near-surface region of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ particles synthesized. The small peak at 1144.2 eV corresponded to a multiplet satellite.

As seen in Figure 4b, the O 1s peak was a doublet. The peak on the lower binding energy side (M−O) at 528.7 eV corresponded to oxygen in the lattice, while that on the higher energy side (V'O) at 530.3 eV was assigned to the defect oxygen. The high relative intensity of the defect oxide peak indicates that several defects existed in Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ because both Eu$^{2+}$ and Eu$^{3+}$ coexisted in the lattice.

2.3. Rietveld Analysis. The Rietveld analysis of the XRD patterns of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ sample was carried out to investigate the occupancy of the Eu$^{2+}$/3+ ions in the Ca$^{2+}$ and the Zr$^{4+}$ sites. The Rietveld refinement profile of the sample is shown in Figure 5, and the crystallographic data and structural refinement parameters are summarized in Tables 1 and 2, respectively. Figure 6 shows the crystal structure of Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ illustrated using the VESTA program based on the crystallographic data from the Rietveld refinement. As shown in Table 1, the low R-factors were obtained for the sample. The Rietveld analysis revealed that the Eu$^{2+}$/3+ ions...
Ca0.7Eu0.3ZrO3 sample as well as the di-

were located in the Ca2+ site, as seen in Table 2. These results occupancy at the O1 site was 0.93, indicating that oxide anion vacancies were formed in the crystal lattice, and the XPS results show that this behavior was more pronounced on the surface.

occupied both Ca2+ and Zr4+ sites and most of the Eu ions were located in the Ca2+ site, as seen in Table 2. These results were in agreement with the results in Figure 2. The ratio of Eu2+ to Eu3+ was 12:1 in the bulk crystal lattice in contrast to 1:4 on the surface determined by XPS. The precision occupancy at the O1 site was 0.93, indicating that oxide anion vacancies were formed in the crystal lattice, and the XPS results show that this behavior was more pronounced on the surface.

The atomic arrangement in the bulk region is neatly aligned than that in the surface region, and there are fewer lattice defects. On the surface of a particle, on the other hand, there are a lot of uncoupled hands (i.e., dangling bonds). The electronic states for dangling bonds are different from those for the aligned structure in the bulk region. In the case of micron-sized particles, the bulk structure is much thicker than the surface structure. Therefore, the electronic states of micron-sized particles are generally different between surface and bulk regions. Additionally, it is previously reported that Eu2+ ions in the outermost layer were easily oxidized to Eu3+.34 In this work, the sizes of the particles obtained were of the order of micrometers, as seen in the FE-SEM images (Figure 3). From the results of the XPS and Rietveld analyses, it was evidenced that Eu2+ and Eu3+ species coexisted in the sample, and the former was dominant within the bulk and the latter was dominant on the surface.

2.4. Reflectance Spectra. The UV–vis reflectance spectra of the Ca1−xEu0.4ZrO3 (0 ≤ x ≤ 0.4) pigments are depicted in Figure 7a. As shown in Figure 7a, high reflectance was observed in the visible light region for the nondoped CaZrO3 (x = 0) sample. In contrast, the Eu2+-doped Ca1−xEu0.4ZrO3 (0.1 ≤ x ≤ 0.4) samples strongly absorbed blue light in the wavelength range from 435 to 480 nm, which is the complementary color of yellow. This optical absorption band was originated by the allowed transition between 4f and 5d orbitals of Eu2+.16

An enlarged view of reflectance spectra from 350 to 500 nm is shown in Figure 7b. In the x range of 0.1 ≤ x ≤ 0.3, the spectral curve shifted to the longer wavelength side as the Eu2+ concentration increased. The red shift of the reflectance curve was caused by the increase in the absorption intensity depending on the Eu2+ content. In the case of the x range of x > 0.3, on the other hand, the spectrum did not shift because the crystal field strength around the Eu2+ ions became weaker due to the lattice expansion. Accordingly, there is a trade-off between the red shift due to the increase in the Eu2+ concentration and the blue shift due to the expansion of the crystal lattice. The results of the reflectance spectra suggest that in Ca1−xEu0.4ZrO3, the red shift effect due to the increase in the absorption intensity of the 4f–5d transition was dominant at 0.1 ≤ x ≤ 0.3, but this effect was offset by the blue shift effect attributed to the reduction of the crystal field energy around Eu2+ ions at x > 0.3.

Figure 7c is an enlarged view of the wavelength region above 550 nm. The reflectance at wavelengths above 600 nm was reduced by Eu2+ doping. This behavior was attributed to the presence of the lattice and surface defects. As already discussed on the XPS and Rietveld analyses, oxide anion deficiencies were formed by the dissolution of Eu3+ into the Zr4+ site of Ca0.7Eu0.3ZrO3. The optical absorption above 600 nm was associated with F-type centers, namely oxide anion defects with two trapped electrons.36,37

2.5. Chromatic Properties. The L*ab*Ch* color coordinate data for the Ca1−xEu0.4ZrO3 (0 ≤ x ≤ 0.4) pigments are summarized in Table 3, and the photographs of these pigments are displayed in Figure 8. The brightness value (L*) decreased as the amount of Eu2+ increased. The redness (a*) and yellowness (b*) values increased in a positive direction. The hue angle values (h°) of the Eu2+-doped Ca1−xEu0.4ZrO3 (0.1 ≤ x) pigments were located in the yellow region of 70 ≤ h° ≤ 105. As seen in Figure 7b, blue light absorption due to the 4f–5d transition was saturated in the x range of 0.3 or more, and yellow light reflection was observed most strongly at
Accordingly, the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment showed the highest $b^*$ and $C$ values among the Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 $\leq$ $x$ $\leq$ 0.4) samples synthesized in this study. This means that this pigment exhibited the brightest yellow color.

The color coordinate data of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment was compared with those of the conventional yellow pigments on the market such as BiVO$_4$ (Dainichiseika Color & Chemicals Mfg.), PbCrO$_4$ (NIC) and ZrSiO$_4$:Pr (Kawamura Chemical), as summarized in Table 4. The photographs of these pigments are also displayed in Figure 9. Although the yellowness value ($b^*$) for the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ ($b^*$ = +70.7) fell short of those for BiVO$_4$ and PbCrO$_4$, it was almost equivalent to that of ZrSiO$_4$:Pr. In addition, the redness value ($a^*$) for the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ ($a^*$ = +11.5) pigment was higher than those of the commercial yellow pigments. In other words, the present pigment possesses the significant feature of a warmer reddish yellow color that is not found in the conventional pigments, although this pigment contains expensive europium.

2.6. Thermal and Chemical Stability Tests. The thermal and chemical stabilities of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment were evaluated using the powder sample. To check the thermal stability, this sample was heated in an aluminum silicate (mullite) crucible at 300 and 500 $^\circ$C for 3 h in an air atmosphere and naturally cooled to room temperature. The acid/base resistance of the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment was tested in 4% CH$_3$COOH and 4% NH$_4$HCO$_3$ aqueous solutions, and the pigment was soaked in the acid solution and the base solution, respectively. After allowing them to stand at room temperature for 2 h, the pigments were washed with deionized water and ethanol and then dried at ambient temperature. The chromatic coordinate data of the samples after the thermal and chemical stability tests are summarized in Table 5.

Unfortunately, thermal stability of this sample was insufficient, and the original color disappeared after heating the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment at 300 $^\circ$C and above in air. This result was attributed to that Eu$^{3+}$ was oxidized to Eu$^{4+}$ by

| atom | site | $g$ | $x$ | $y$ | $z$ | $B_m$/Å$^2$ |
|------|------|-----|-----|-----|-----|-------------|
| Ca   | 4c   | 0.7225$^b$ | 0.04498(14) | 1/4 | 0.4900(3) | 0.66 |
| Eu1(Eu$^{3+}$) | 4c | 0.2775(6) | $x$(Ca) | $y$(Ca) | $z$(Ca) | 0.66 |
| Zr   | 4a   | 0.9775$^b$ | 0 | 0 | 0 | 0.23 |
| Eu2(Eu$^{3+}$) | 4a | 0.0225 | 0 | 0 | 0 | 0.23 |
| O1   | 4c   | 0.929(7) | 0.4639(9) | 1/4 | 0.5966(8) | 0.51 |
| O2   | 8d   | 1 | 0.2887(7) | 0.0573(4) | 0.2052(7) | 0.51 |

$^a$The isotropic atomic displacement parameters ($B_m$) of calcium, zirconium, and oxygen sites were fixed to 0.66, 0.23, and 0.51 Å$^2$, respectively, with reference to the literature.$^{25-26}$ $^b$The occupancies ($g$) of the Ca and Zr sites were linearly constrained: $g$(Ca) = 1 − $g$(Eu1), $g$(Eu2) = 0.3 − $g$(Eu1), and $g$(Zr) = 1 − $g$(Eu2).

Figure 6. Crystal structure obtained by the Rietveld analysis for Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ (Eu$^{3+}$: yellow, Eu$^{4+}$: blue).
Table 3. Chromatic Parameters for the Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ x ≤ 0.4) Samples

| $x$  | $L^*$ | $a^*$ | $b^*$ | $C$  | $h^*$ |
|------|-------|-------|-------|------|-------|
| 0    | 96.4  | −0.39 | +2.24 | 2.27 | 99.9  |
| 0.10 | 83.5  | +4.61 | +52.7 | 52.9 | 85.0  |
| 0.20 | 74.1  | +10.8 | +63.6 | 64.5 | 80.4  |
| 0.25 | 71.8  | +12.0 | +68.5 | 69.5 | 80.1  |
| 0.30 | 71.3  | +11.5 | +70.7 | 71.6 | 80.8  |
| 0.35 | 68.8  | +10.8 | +69.5 | 70.3 | 81.2  |
| 0.40 | 68.6  | +10.3 | +69.1 | 69.9 | 81.5  |

3. CONCLUSIONS

Eu$^{2+}$-doped calcium zirconates, Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ x ≤ 1), were synthesized using a solid-state reaction method as environmentally benign inorganic yellow pigments. The samples strongly absorbed the blue light at the wavelengths of 435–480 nm by the 4f–5d transition of Eu$^{2+}$. As a result, the samples showed bright yellow, and the brightest yellow color was obtained with the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ ($a^* = +11.5, b^* = +70.7$) sample. The yellowness value ($b^*$) of this pigment was almost equal to that of the commercially available prasemium yellow pigment. In addition, the redness value ($a^*$) was larger than that of the commercial one. Accordingly, the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment exhibited a warmer reddish yellow color. Although heat resistance of this pigment was not enough, this pigment has chemical stability. Since Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ is composed only of nontoxic elements, it is expected to be one of the environmentally friendly inorganic yellow pigment series.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. The Ca$_{1-x}$Eu$_x$ZrO$_3$ (0 ≤ x ≤ 1) samples were synthesized by a conventional solid-state reaction method. CaCO$_3$ (99.5%), Eu$_2$O$_3$ (99.999%), and ZrO$_2$ (98.7%) powders were used as the starting materials. Stoichiometric amounts of each reagent were mixed in an agate mortar. The mixtures were calcined in an alumina boat at 1400 °C for 10 h in a flow of 5% H$_2$–95% N$_2$ mixed gas. Finally, the samples were ground in an agate mortar before characterization.

4.2. Characterization. The samples synthesized were characterized by the following methods. X-ray fluorescence spectroscopy (Rigaku, ZSX Primus) measurements indicated that the sample compositions were in good agreement with the nominal stoichiometric compositions of the starting mixtures. The crystal structure of the sample was identified by XRD (Rigaku, Ultima IV) with Cu K$\alpha$ radiation, operated with voltage and current settings of 40 kV and 40 mA, respectively. The XRD data were collected by scanning a 2$\theta$ range of 20–80°. The lattice volume was calculated with the CellCalc Ver 2.20 software from the refined XRD peak angles using α-Al$_2$O$_3$ as a standard. Rietveld refinement of the resulting XRD patterns obtained in the 2$\theta$ range from 10° to 120° was performed by the RIETAN-FP software package to determine the precise crystal structure and also to investigate the occupancy of Eu$^{2+}$/3+ at Ca$^{2+}$ and Zr$^{4+}$ sites in Ca$_{1-x}$Eu$_x$ZrO$_3$. From the Rietveld analysis, the final reliability factors ($R$-factors) were obtained: weighted pattern $R$-factor ($R_w$), $R$-expected factor ($R_e$), goodness-of-fit ($S$), and R-structure factor ($R_s$). XPS (ULVAC-PHI, PHI5000 Versa Probe II) was measured using Al K$\alpha$ radiation to investigate the electronic state of Eu and O in the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ sample.

The size and morphology of the Ca$_{1-x}$Eu$_x$ZrO$_3$ ($x = 0.1, 0.2, 0.3, 0.4$) samples were observed using FE-SEM (JEOL, JSM-6701F). The optical reflectance spectra of the samples were measured with an ultraviolet–visible–near infrared spectrometer (JASCO, V-770) with reference to a standard white plate. The color properties of the samples were evaluated on the Commission Internationale de L’Eclairage (CIE) $L^*a^*b^*$ system using a colorimeter (Konica-Minolta, CR-300). The $L^*$ parameter describes the brightness of a color with respect to neutral grayscale, and the $a^*$ (the red–green axis) and $b^*$ (the yellow–blue axis) parameters quantitatively.

heating in air. The color degradation was caused by the significant decrease in the absorption intensity of 4f–5d transition. However, the present pigment can be unproblematically used to the general application such as paints because common pigments have been mostly used at about room temperature.$^{41,42}$ On the other hand, the color was almost unchanged after the leaching test in the acid and the base solutions. Therefore, the Ca$_{0.7}$Eu$_{0.3}$ZrO$_3$ pigment has chemical stability.
describe the color. The chroma parameter \(C\), which represents the color saturation of the pigment, is calculated by the following formula: \(C = [(a^*)^2 + (b^*)^2]^{1/2}\). The parameter \(h^o\) ranges from 0 to 360 (70 \(\leq h^o \leq 105\) means yellow) and is calculated by the formula, \(h^o = \tan^{-1}(b^*/a^*)\).

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Notes
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# REFERENCES

(1) Těšťelová, K.; Šucová, P. Synthesis and Study of Bi₂CeO₇ as Inorganic Pigment. J. Therm. Anal. Calorim. 2016, 125, 1047—1052.
(2) Šucová, P.; Trojan, M. Thermal Synthesis and Properties of the (Bi₂O₃)₁₋ₓ(H₂O)ₓ Oxides. J. Therm. Anal. Calorim. 2006, 83, 557—559.
(3) Cai, M.; Chen, S.; Ma, X.; Chen, J. New Environmental-Friendly Yellow Pigments \(Y_{a-x}A_{x}MoO_{b+6}\) (\(A = Ta, Tb\)). J. Rare Earths 2019, 37, 741—749.
(4) Kusumoto, K. Synthesis of Bi₂O₃-Nb₂O₅ Solid Solutions for Environmental-Friendly Reddish Yellow Pigments. J. Ceram. Soc. Jpn. 2018, 124, 926—928.
(5) Guo, D.; Yang, Q.; Chen, P.; Chu, Y.; Zhang, Y.; Rao, P. The Influence of Micronization on the Properties of Pr-ZrSiO₄ Pigment. Dyes Pigm. 2018, 153, 74—83.
(6) Nero, G. D.; Cappelletti, G.; Ardizzone, S.; Ferrero, P.; Giglioni, S. Yellow Pr-Zircon Pigments: The Role of Praseodymium and of the Mineralizer. J. Eur. Ceram. Soc. 2004, 24, 3603—3611.
(7) Masui, T.; Honda, T.; Wendumu; Imanaka, N. Novel and Environmentally Friendly \((Bi, Ca, Zn)VO₃\) Yellow Pigments. Dyes Pigm. 2013, 99, 636—641.
(8) Masui, T.; Tategaki, H.; Furukawa, S.; Imanaka, N. Synthesis and Characterization of New Environmentally-Friendly Pigments Based on Cerium Phosphate. J. Ceram. Soc. Jpn. 2004, 112, 646—649.
(9) Imanaka, N.; Masui, T.; Itaya, M. Synthesis of an Environmentally Friendly and Nontoxic New Pigment Based on Rare Earth Phosphate. Chem. Lett. 2003, 32, 400—401.
(30) Cho, E.-J.; Oh, S.-J.; Imada, S.; Suga, S.; Suzuki, T.; Kasuya, T. Origin of the high-binding-energy structure in the 3d core-level spectra of divalent Eu compounds. Phys. Rev. B 1995, 51, 10146–10149.
(31) Cho, E.-J.; Oh, S.-J. Surface Valence Transition in Trivalent Eu Insulating Compounds Observed by Photoelectron Spectroscopy. Phys. Rev. B 1999, 59, R15613–R15616.
(32) Cabello, G.; Lillo, L.; Caro, C.; Buono-Core, G. E.; Chornik, B.; Flores, M.; Carrasco, C.; Rodriguez, C. A. Photochemical Synthesis of AZrO3−x Thin Films (A = Ba, Ca and Sr) and Their Characterization. Ceram. Int. 2014, 40, 7761–7768.
(33) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272–1276.
(34) Ohno, Y.; Urata, T. Photoelectron Spectra and Surface Valence Fluctuation of Eu in the Misfit-Layer compound [(EuS)1.15]1.5NbS2. J. Electron Spectrosc. Relat. Phenom. 2002, 125, 171–180.
(35) Dorenbos, P. Energy of the First 4f7 → 4f65d Transition of Eu2+ in Inorganic Compounds. J. Lumin. 2003, 104, 239–260.
(36) Wachsmann, E. D.; Jiang, N.; Frank, C. W.; Mason, D. M.; Stevenson, D. A. Spectroscopic Investigation of Oxygen Vacancies in Solid Oxide Electrolytes. Appl. Phys. A 1990, 50, 545–549.
(37) Wright, D. A.; Thorp, J. S.; Aygar, A.; Buckley, H. P. Optical Absorption in Current-Blackened Yttria-Stabilized Zirconia. J. Mater. Sci. 1973, 8, 876–882.
(38) Furukawa, S.; Masui, T.; Imanaka, N. Synthesis of New Environment-Friendly Yellow Pigments. J. Alloys Compd. 2006, 418, 255–258.
(39) Furukawa, S.; Masui, T.; Imanaka, N. New Environment-Friendly Yellow Pigments Based on CeO2−ZrO2 Solid Solutions. J. Alloys Compd. 2008, 451, 640–643.
(40) Sumaletha, N.; Rajesh, K.; Mukundan, P.; Warrier, K. G. K. Environmentally Benign Sol-Gel Derived Nanocrystalline Rod Shaped Calcium Doped Cerium Phosphate Yellow-Green Pigment. J. Sol-Gel Sci. Technol. 2009, 52, 242–250.
(41) Buxbaum, G.; Pfaff, G. Industrial Inorganic Pigments, 3rd ed.; Wiley-VCH: Weinheim, 2005.
(42) Smith, H. M. High Performance Pigments; Wiley-VCH: Weinheim, 2003.
(43) Izumi, F.; Momma, K. Three-Dimensional Visualization in Powder Diffraction. Solid State Phenom. 2007, 130, 15–20.