1. Introduction

Inorganic pigments composed of metal oxides are applied in a wide range of products such as paints, ceramics, plastics and road marking, due to their high thermal and ultraviolet stability compared to organic pigments.11) As yellow pigments, cadmium yellow (CdS) and chromium yellow (PbCrO₄) have been popularly used as conventional inorganic pigments. However, the use of these pigments has been restricted because they contain harmful elements (e.g. Cd, Pb, and Cr), which have deleterious effect on the human body and the environment. It has been reported that a lot of people die each year due to lead poisoning;12) chromium trioxide has tendency to cause malformation in chick embryos;13) and cadmium intoxication damages the basal ganglia resulting in Parkinsonism.4) Accordingly, the use of the conventional pigments containing these toxic elements are strictly limited by the Restriction of Hazardous Substances (RoHS) directive, etc. Therefore, the development of alternative environmentally friendly inorganic pigments are strongly requested.

Because of this situation, a number of studies have been reported on inorganic yellow pigments without using toxic elements.5)–21) Among them, tetravalent lanthanide ions (Ce⁴⁺, Pr⁴⁺, and Tb⁴⁺) have been remarked particularly, because the pigments containing them show optical absorption of blue light based on the charge transfer transition from O₂p to Ln⁴f. In fact, non-toxic CeO₂-ZrO₂-B₂O₃;22) ZrSiO₄:Pr;20) and Sr₂Ce₁₋ₓSnₓO₃ (Ln = Ce, Tb, Pr)²₄) pigments have been proposed for examples of the environmentally friendly yellow pigments.

In this study, we focused on the perovskite-type oxides containing tetravalent rare earth ions. The general formula is A₂Ln₃O₁₂ (A = Ca, Sr, Ba; Ln = Ce, Pr, Tb), where A has a larger ionic size than that of B. The stability is often estimated by the tolerance factor (t), which was introduced by Goluschmidt in 1920, and where rₐ, rₜ, and rₒ²⁻ are the ionic radii of cation A, B, and anion O²⁻, respectively. The ideal perovskite without distortion should show t = 1.0, and the t value of most perovskite-type oxides is empirically in the range of 0.75 to 1.0.²²) Here, those of A₂Ln₃O₁₂ (A = Ca, Sr, Ba; Ln = Ce, Pr, Tb) falls within this range, and it is expected that these oxides can form stable perovskite-type structure. Although a patent has been reported as prior research, there is no detailed data other than color characterization of the terbium-containing compounds.²³) Similar perovskite-type compounds such as SrSn₀.₆Ca₀.₄O₃ (Ln = Ce, Tb, Pr)²₄) and BaSn₁₋ₓTbxO₃ (x = 0.2)²₅) have also been reported, but, unfortunately, these pigments contain harmful tin. In this study, therefore, A₂Ln₃O₁₂ (A = Ca, Sr, Ba; Ln = Ce, Pr, Tb) were synthesized by a solid state reaction method, and the pigments were characterized by using X-ray powder diffraction and UV–Vis spectroscopy, as well as color properties.

2. Experimental procedure

2.1 Materials and methods

The A₂Ln₃O₁₂ (A = Ca, Sr, Ba; Ln = Ce, Pr, Tb) pigments were synthesized using a conventional solid-state reaction method. CaCO₃ (99.9%), SrCO₃ (95.0%), BaCO₃ (99.0%), CeO₂ (99.9%), Pr₂O₃ (99.9%) and Tb₂O₃ (99.9%) powders were used as starting materials. Stoichiometric amounts of alkaline earth metal carbonates and lanthanide oxides were mixed in an agate mortar. The mixtures were calcined in an alumina boat at 1373 K for 3 h under an air atmosphere. Finally, the samples were ground in an agate mortar before characterization.

2.2 Characterization

X-ray fluorescence spectroscopy (XRF; Rigaku, ZSX Primus) measurements indicated that the sample compositions were in good agreement with the nominal stoichiometric compositions of the starting materials. The samples were characterized by X-ray powder diffraction (XRD; Rigaku, Ultima IV) with Cu-Kα radiation (40 kV and 40 mA) to identify their crystal structures. The data were collected by step scanning over a 2θ range from 20 to 80° with a step size of 0.02° at a scan rate of 6° min⁻¹.

The optical reflectance of the samples was measured with a
UV–Vis spectrometer (Shimadzu, UV-2550) using barium sulfate as a reference. The bandgap energies of the samples were determined from the absorption edge of the absorbance spectra represented by the Kubelka–Munk function, \( f(R) = (1 - R^2)/2R \), where \( R \) is reflectance.\(^{25}\) The color properties of the samples were estimated in terms of the CIE \( L^*a^*b^*Ch^o \) system with a colorimeter (Konika-Minolta, CR-300). This color measurement was made for powder samples. The value \( L^* \) indicates the brightness or darkness of a color relative to a neutral grey scale, and the values of \( a^* \) (the axis red-green) and \( b^* \) (the axis yellow-blue) represent the color hue. Chroma parameter \( C \) represents the color saturation of the pigments and is calculated with the formula: \( C = [(a^*)^2 + (b^*)^2]^{1/2} \). The parameter \( h^o \) ranges from 0 to 360°, and is calculated according to the following formula: \( h^o = \tan^{-1}(b^*/a^*) \).

3. Results and discussion

3.1 \( \text{ACeO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \))

Figure 1 shows the XRD patterns of the \( \text{ACeO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \)) pigments. \( \text{SrCeO}_3 \) and \( \text{BaCeO}_3 \) were obtained in a single-phase form. In the case of \( \text{CaCeO}_3 \), however, a mixture of \( \text{CaO} \) and \( \text{CeO}_2 \) was obtained. Since the ionic radius of \( \text{Ca}^{2+} \) (ionic radius: 0.175 nm),\(^{26} \) the tolerance factor \( t \) of \( \text{CaCeO}_3 \) \( (t = 0.85) \) is greatly deviated from the ideal value \( (t = 1) \). Therefore, the crystal structure of \( \text{CaCeO}_3 \) is strongly distorted and the perovskite-type structure is not stable, although it is within the allowable range according to the above empirical rule.

The UV–Vis diffuse reflectance spectra for the \( \text{ACeO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) samples obtained in a single-phase form are depicted in Fig. 2. Optical absorption due to the \( \text{O}_2\text{p–Ce}_4\text{f} \) charge transfer transitions\(^{27}\) was observed at a wavelength of 400 nm or less for the \( \text{ACeO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) samples. In addition, small and broad shoulder bands were also observed in the visible light region from 400 to 750 nm in both samples, which were associated with F-type centers, namely oxygen vacancies with one or two trapped electrons.\(^{28}\) The chromatic parameters of the \( \text{ACeO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) samples are summarized in Table 1. Both samples showed high \( L^* \) value. The \( a^* \) values were close to 0, but the \( b^* \) values were slightly positive. As a result, the color of the \( \text{ACeO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) samples was ivory white.

3.2 \( \text{APrO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \))

The XRD patterns of the \( \text{APrO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \)) samples are shown in Fig. 3. Among these samples, a single-phase perovskite structure was obtained for the \( \text{BaPrO}_3 \) sample only. In contrast, \( \text{CaPrO}_3 \) and \( \text{SrPrO}_3 \) were obtained as mixtures of multiple phases. Since the tolerance factors \( t \) of \( \text{CaPrO}_3 \) and \( \text{SrPrO}_3 \) are 0.86 and 0.89, respectively, it is not stable for them to adopt the perovskite-type structure for the same reason mentioned in the case of \( \text{CaCeO}_3 \).

Figure 4 shows the UV–Vis diffuse reflectance spectrum of the \( \text{BaPrO}_3 \) sample obtained in a single-phase form. The \( \text{BaPrO}_3 \) sample exhibited strong optical absorption at a wavelength of 450 nm and shorter, which is attributed to the charge transfer transition between the \( \text{O}_2\text{p} \) and \( \text{Pr}_4\text{f} \) orbitals.\(^{29,30} \) The \( L^*a^*b^*Ch^o \)
color coordinate data for the BaPrO₃ pigment are also listed in Table 1. The BaPrO₃ pigment shows a relatively high \( b^* \) value, but it was dark brown due to the low \( L^* \) and positive \( a^* \) values.

### 3.3 \( \text{ATbO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \))

The XRD patterns of the \( \text{ATbO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \)) samples are shown in Fig. 5. A single phase of the perovskite-type structure was observed for the SrTbO₃ and BaTbO₃ samples, while CaTbO₃ was obtained as a mixture of CaO and Tb₄O₇. As the tolerance factor (\( t \)) of CaTbO₃ is 0.90, it was unstable due to the same reason mentioned in the case of CaCeO₃, CaPrO₃, and SrPrO₃.

The UV–Vis diffuse reflectance spectra for the \( \text{ATbO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) samples obtained in a single-phase form are depicted in Fig. 6. Both samples exhibited strong optical absorption at wavelengths between 435 and 470 nm (i.e., in the blue light region), corresponding to the O₂p–Tb₄f charge transfer transitions. The samples are yellow, because blue is a complementary color of yellow.

### 3.4 Comparison with commercially available pigments

The UV–Vis diffuse reflectance spectra for the \( \text{ATbO}_3 \) (\( A = \text{Sr}, \text{Ba} \)) were compared to those for the commercially available praseodymium yellow (ZrSiO₄:Pr, Kawamura Chemical) and bismuth vanadate (BiVO₄, Dainichiseika Color & Chemicals Manufacturing), as shown in Fig. 7. Their absorption spectra represented by the Kubelka-Munk function are also depicted in Fig. 8. They were compared using powder samples. It was found that all the samples selectively absorbed light on the shorter wavelength side than 480 nm (\( \leq 2.58 \text{ eV} \)) corresponding to blue color and strongly reflected light on longer wavelength side. As a result, the SrTbO₃ and BaTbO₃ samples were colored yellow.

The color parameters of these pigments are summarized in Table 2. The bandgap energies were obtained by the extrapolation of the linear portions to zero absorption in Fig. 8, and they are also listed in this table. The photographs of these pigments are also displayed in Fig. 9 with those of SrCeO₃, BaCeO₃, and BaPrO₃ as references. The yellowness value for SrTbO₃ (\( b^* = +69.4 \)) was even equal to that of ZrSiO₄:Pr. In addition, the greenness value for the former (\( a^* = -9.34 \)) was higher than that of the latter. Accordingly, the SrTbO₃ sample was more greenish than ZrSiO₄:Pr. In the case of the BaTbO₃ pigment, on the other hand, the yellowness value (\( b^* = +79.9 \)) was even equal to that of BiVO₄, while the \( a^* \) value was significantly closer to 0, due to the smallest bandgap energy. Therefore, the BaTbO₃ pigment showed a purer yellow color than BiVO₄.

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**Fig. 4.** UV–Vis diffuse reflectance spectrum of the BaPrO₃ sample.

**Fig. 5.** XRD patterns of the \( \text{ATbO}_3 \) (\( A = \text{Ca}, \text{Sr}, \text{Ba} \)) samples.

**Fig. 6.** UV–Vis diffuse reflectance spectra of the SrTbO₃ and BaTbO₃ samples.

**Fig. 7.** UV–Vis diffuse reflectance spectra for SrTbO₃, BaTbO₃, and commercial yellow pigments.
Table 3: CIE-\(L^{*}a^{*}b^{*}Ch^{*}\) color coordinate and optical bandgap energies (\(E_{g}\)) of SrTbO\(_3\), BaTbO\(_3\), and commercial ZrSiO\(_4\):Pr and BiVO\(_4\) yellow pigments

| Pigment     | \(L^{*}\) | \(a^{*}\) | \(b^{*}\) | \(C\) | \(h^{*}\) | \(E_{g}/eV\) |
|-------------|----------|----------|----------|--------|---------|-------------|
| SrTbO\(_3\) | 83.0     | -9.34    | 69.4     | 70.0   | 97.7    | 2.47        |
| BaTbO\(_3\) | 87.1     | -1.03    | 79.9     | 79.9   | 90.7    | 2.38        |
| ZrSiO\(_4\):Pr | 83.5 | -3.28    | 70.3     | 70.4   | 92.7    | 2.42        |
| BiVO\(_4\)  | 93.3     | -15.7    | 80.3     | 81.8   | 101     | 2.51        |

Fig. 9. Photographs of SrTbO\(_3\) (a), BaTbO\(_3\) (b), ZrSiO\(_4\):Pr (c), BiVO\(_4\) (d), SrCeO\(_3\) (e), BaCeO\(_3\) (f), and BaPrO\(_3\) (g).

3.5 Chemical stability tests

The chemical stability of the SrTbO\(_3\) and BaTbO\(_3\) pigments was evaluated using the powder samples. The pigment powders were dispersed into 4% acetic acid and 4% ammonium bicarbonate. After leaving them at room temperature for 2h, the sample was washed with deionized water and ethanol, and then dried at room temperature. The color of the pigment after the leaching test was evaluated using the colorimeter. As shown in Table 3, the color of the present SrTbO\(_3\) and BaTbO\(_3\) pigments was almost unchanged in the basic ammonium bicarbonate solution, but unfortunately, the color degradation was observed by soaking them in the acetic acid solution. Therefore, surface coating with a stable compound such as silica is suggested to be necessary for them to apply for the pigments.

4. Conclusions

Perovskite-type ALnO\(_3\) (\(A = \text{Ca, Sr, Ba}; Ln = \text{Ce, Pr, Tb}\)) oxides were synthesized as environmentally friendly inorganic yellow pigments. The colors of \(A\text{CeO}_{2}\) (\(A = \text{Sr, Ba}\)), BaPrO\(_3\), SrTbO\(_3\), and BaTbO\(_3\) obtained in a single phase form were ivory white, dark brown, greenish yellow, and pure yellow, respectively. In particular, SrTbO\(_3\) and BaTbO\(_3\) showed high yellowness values. The bandgap energies of SrTbO\(_3\) and BaTbO\(_3\) were 2.47\(eV\) and 2.38\(eV\), respectively, and the yellowness of the former was even equal to that of praseodymium yellow, while that of the latter was that of bismuth vanadate. However, color degradation of the SrTbO\(_3\) and BaTbO\(_3\) pigments was observed by soaking them in a diluted acetic acid solution.

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