Synthesis and characterisation of SrY_{2-x}Ce_xO_4 as environmentally friendly reddish-brown pigments

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Reddish-brown SrY_{2-x}Ce_xO_4 (0 \leq x \leq 1.2) solid solutions were synthesized by a citrate sol–gel method as novel environmentally friendly inorganic pigments. The powders obtained were characterized by X-ray powder diffraction (XRD), UV-vis diffuse reflectance spectra and CIE L*a*b*Ch* chromatic coordinate measurements. All SrY_{2-x}Ce_xO_4 (0 \leq x \leq 1.2) samples were obtained in a single-phase form and the lattice volume increased on increasing the Ce^{3+} concentration. The reddish-brown pigments exhibited optical absorption due to the 4f–5d allowed transition of Ce^{3+}. The absorption bands observed in the wavelength region of 400 and 550 nm were due to the Ce^{3+} ions in the ideal octahedral Y^{3+} site and those in the longer wavelength region above 600 nm were attributed to the transition of Ce^{3+} in the distorted octahedral Y^{3+} site. The samples gradually became reddish on increasing the Ce^{3+} content. The most reddish colour was obtained in SrYCeO_4 (a* = +21.8).

Introduction

Inorganic pigments are typically applied to ceramic tiles, inks and paints, due to their high hiding power, weather resistance and thermal stability. However, the use of the conventional pigments containing toxic elements, such as Cd, Pb, Hg, Cr, Co, and Sb, has been forbidden or restricted, because they have adverse effects on the human body and the environment. Therefore, a number of non-toxic inorganic pigments have been reported by several researchers in order to replace the toxic pigments with the environmentally-friendly or less-toxic ones. In particular, development of novel red pigments has been required and several studies have been reported. Among them, it has been reported that CaFe_{2}O_{4}–Ni_{1+x} and Ce_{3}S_{2} showed bright red colour. But, unfortunately, harmful NO_{x} and SO_{x} are generated when these nitride and sulphide pigments are incinerated. Therefore, oxides are desirable as materials for environmentally friendly pigments.

Because of this situation, we focused on a trivalent cerium (Ce^{3+}) ion as a red colouring source. As an example of a popular Ce^{3+}-containing material, Ce^{3+}-doped yttrium aluminium garnet, (Y, Ce)_3Al_5O_12 (YAG:Ce^{3+}), has been well known as a yellow-emitting phosphor widely used in white light emitting diodes. YAG:Ce^{3+} absorbs the visible lights in the wavelength region of 410–500 nm which is attributed to the 4f–5d allowed transition. The absorption wavelength due to the Ce^{3+} ions depends on the host crystal structure, because the energy level of the 5d orbital of Ce^{3+} is strongly affected by the crystal field strength around the Ce^{3+} ions. In the case of a phosphor, the amount of Ce^{3+} is about 1 mol% to prevent concentration quenching, but it is considered that colouring of the sample can be seen by further increasing the Ce^{3+} concentration. Furthermore, it is expected that strong reddish colour will be obtained if Ce^{3+} is doped at a high concentration in the Y^{3+} site in the lattice with a stronger crystal field.

In this study, we selected SrY_{2}O_{3} as a host material, because this compound is composed of non-toxic elements. SrY_{2}O_{3} belongs to the CaFe_{2}O_{4}-related structure, and it crystallizes into an orthogonal structure with space group Pnma. Four formula units for a total of 28 atoms are contained in the SrY_{2}O_{3} structure. All of the constituent atoms occupy 4c sites according to the Wyckoff notation. The Sr^{2+} and Y^{3+} ions are coordinated by eight and six O^{2−} ions, respectively. Y^{3+} occupies two non-equivalent sites C_{a} symmetry, where one Y(1) site is nearly a regular octahedron but the other Y(2) one is much distorted. Since it has been reported that high calcination temperature is necessary for the synthesis of SrY_{2}O_{3} by a solid-state reaction, SrY_{2-x}Ce_xO_4 (0 \leq x \leq 1.2) pigments were synthesized using a citrate sol–gel method. The optical and colour properties of the samples were evaluated as novel environmentally friendly inorganic reddish-brown pigments.

Experimental

Materials and methods

The SrY_{2-x}Ce_xO_4 (0 \leq x \leq 1.2) pigments were synthesized using a citrate sol–gel method. Sr(NO_{3})_2 (Wako Pure Chemical Industries Ltd., 99.9%), Y(NO_{3})_3·6H_{2}O (Kishida Chemical Co.
VersaProbe II) using Mg-K \( a \) calculated with the formula, 

\[ \text{mole ratio } 2 : 1 \text{ with respect to the total cations (Sr, Y and Ce).} \]

A chelating agent to complex the cations into the solution in the solution was stirred homogeneously, citric acid was added as the dried gel was calcined in an aluminium silicate (mullite) crucible at 500 °C for 6 h in air. After the calcination, the sample was heated again at 1300 °C for 6 h in a flow of 5% \( \text{H}_2 – 95\% \text{ N}_2 \) gas. Before characterisation, the sample was ground in an agate mortar.

### Characterisation

The samples synthesized were characterised by X-ray powder diffraction (XRD; Rigaku, Ultima IV) with Cu-K \( a \) radiation, operated with voltage and current settings of 40 kV and 40 mA, respectively. The sampling width and the scan speed were 0.02° and 6° min \(^{-1}\). The lattice parameters and volumes were calculated from the XRD peak angles, which were refined using \( \alpha \)-Al\( \text{2O}_3 \) as a standard and using the CellCalc Ver. 2.20 software.

Rietveld refinement of the obtained XRD patterns was performed using the RIETAN-FP software package to determine the precise crystal structure and the occupancy of the Y(1) and the Y(2) sites for the \( \text{SrY}_2 \_ \text{CeO}_4 \) \((x = 0, 0.2, 1.0) \) samples. From the Rietveld refinement, the following final \( R \)-factors were obtained: \( R_w \) (\( W \)-weighted pattern), \( R_p \) (\( P \)-pattern), \( R_e \) (\( E \)-expected), \( S \) (goodness-of-fit indicator), and \( R_F \) (\( F \)-structure factor).

The morphology of the \( \text{SrY}_2 \_ \text{CeO}_4 \) particles was investigated by using field-emission-type scanning electron microscopy (FE-SEM; JEOL, JSM-6701F). The optical reflectance spectra were measured with a UV-vis spectrometer (Shimadzu, UV-2550 with an integrating sphere attachment) with barium sulphate as a reference. The colour properties of the samples were evaluated in terms of the CIE \( L^*a^*b^*Ch \) system using a chromometer (Konica-Minolta, CR-300). The \( L^* \) parameter indicates the brightness or darkness of a colour relative to a neutral grey scale, and the \( a^* \) (the red-green axis) and \( b^* \) (the yellow-blue axis) parameters express the colour qualitatively. Chroma parameter \( (C) \) represents the colour saturation of the pigments and is calculated according to the following formula: \( C = [(a^*)^2 + (b^*)^2]^{1/2} \). The parameter \( h^* \) ranges from 0 to 360°, and is calculated with the formula, \( h^* = \tan^{-1}(b^*/a^*) \). X-ray photoelectron spectra measurements (XPS; ULVAC-PHI, PHI5000 VersaProbe II) using Mg-K\( a \) radiation were carried out to investigate the oxidation state of the cerium ion on the surface of the as-synthesized and the calcined \( \text{SrY}_2 \_ \text{CeO}_4 \) samples.

### Results and Discussion

#### X-ray powder diffraction and SEM image

Fig. 1 shows the XRD patterns of the synthesized \( \text{SrY}_{2-x} \_ \text{CeO}_4 (0 \leq x \leq 1.2) \) pigments. All \( \text{SrY}_{2-x} \_ \text{CeO}_4 (0 \leq x \leq 1.2) \) samples were obtained in a single-phase form, and no diffraction peaks of impurities or other phases were observed in the patterns. The XRD peaks shifted to lower angle direction with increasing the \( \text{Ce}^{3+} \). The lattice volumes of all samples were calculated from the XRD peak angles, and the results are summarized in Table 1. The cell volume increased with increasing the \( \text{Ce}^{3+} \) concentration. These results indicate that \( \text{Y}^{\text{3+}} \) (ionic radius: 0.104 nm)\(^{36} \) ions in the host lattice were partially substituted by larger \( \text{Ce}^{3+} (0.115 \text{ nm}) \) ions to form solid solutions.

The Rietveld analysis of the XRD data of the \( \text{SrY}_{2-x} \_ \text{CeO}_4 (x = 0, 0.2, 1.0) \) samples was carried out to determine the site occupancy of the Y(1) and the Y(2) sites. The Rietveld refinement profiles of the samples are shown in Fig. 2, and the detailed crystallographic data and structure refinement parameters are summarized in Tables 2 and 3, respectively.

### Table 1: Lattice volumes of \( \text{SrY}_{2-x} \_ \text{CeO}_4 (0 \leq x \leq 1.2) \)

| x    | Lattice volume/nm\(^3\) |
|------|------------------------|
| 0    | 0.410                  |
| 0.2  | 0.411                  |
| 0.4  | 0.413                  |
| 0.6  | 0.414                  |
| 0.8  | 0.418                  |
| 1.0  | 0.420                  |
| 1.2  | 0.422                  |
Fig. 3 shows the crystal structure of SrY$_2$O$_4$ illustrated using the VESTA program based on the crystallographic data from the Rietveld refinement.

As seen in Table 2, the low R-factors were obtained for all the SrY$_2$/Ce$_x$O$_4$ ($x = 0, 0.2, 1$) samples. The Rietveld refinements revealed that the Ce$^{3+}$ concentrations at the Y(1) site gradually increased from 16 to 64 mol%, while that in the Y(2) site increased from 4 to 36 mol% as $x$ increased from 0.2 to 1, as seen in Table 3. Therefore, in the SrY$_2$Ce$_x$O$_4$ structure, Ce$^{3+}$ ions occupied both Y(1) and Y(2) sites. Although each Y site is coordinated by six oxide anions, one Y(1) site is located in the ideal octahedral coordination environment and the other Y(2) site is significantly distorted, as shown in Fig. 3.

### Table 2

Crystallographic parameters of SrY$_{2-x}$Ce$_x$O$_4$ ($x = 0, 0.2, 1$) obtained from Rietveld refinement analysis$^a$

| $x$ | Cell data | $R$ factor |
|-----|-----------|------------|
| 0   | $a$ (nm)  | 1.008700(5) | 1.03202(1) |
|     | $b$ (nm)  | 0.34514(2) | 0.36578(4) |
|     | $c$ (nm)  | 1.193350(7) | 1.20445(1) |
|     | $V$ (nm$^3$) | 0.411091(4) | 0.421491(8) |
| 0.2 | $R_{wp}$  | 3.398      | 3.781      |
|     | $R_F$     | 2.662      | 3.119      |
| 1   | $S$       | 1.277      | 2.163      |
|     | $R_B$     | 1.456      | 3.701      |

$^a$ Crystal symmetry: orthorhombic, space group: $Pnma$, number of formula units per unit cell: $Z = 4$.

### Table 3

Refined structural parameters of SrY$_{2-x}$Ce$_x$O$_4$ ($x = 0, 0.2, 1$) pigments from Rietveld refinement using XRD data obtained at room temperature$^a$

| $x$ = 0 $^b$ SrY$_2$O$_4$ | Atom | Occupancy | $x$  | $y$  | $z$  | $U_{iso}$ (nm$^2$) |
|-------------------------|------|-----------|-----|-----|-----|------------------|
| Sr 1                    | 0.24722(9) | 1/4 | 0.64940(9) | 0.0000872(2) |
| Y1 1                    | 0.0775(1)  | 1/4 | 0.38967(7)  | 0.000067(3)  |
| Y2 1                    | 0.5762(1)  | 1/4 | 0.61230(7)  | 0.0000860(3) |
| O1 1                    | 0.2861(5)  | 1/4 | 0.3235(4)   | 0.0001303    |
| O2 1                    | 0.3729(5)  | 1/4 | 0.0193(5)   | 0.0001303    |
| O3 1                    | 0.4852(5)  | 1/4 | 0.7820(4)   | 0.0001303    |
| O4 1                    | 0.07423(6) | 1/4 | 0.0767(4)   | 0.0001303    |

| $x = 0.2$ $^b$ SrY$_{1.8}$Ce$_{0.2}$O$_4$ | Atom | Occupancy | $x$ | $y$ | $z$ |
|----------------------------------------|------|-----------|-----|-----|-----|
| Sr 1                                   | 0.2483(1) | 1/4 | 0.64917(1) |
| Y1 1                                   | 0.0772(1)  | 1/4 | 0.3891(1)  |
| Y2 1                                   | 0.5780(2)  | 1/4 | 0.6125(1)  |
| Ce1 1                                  | 0.04     | 1/4 | 0.3891    |
| Ce2 1                                  | 0.04     | 1/4 | 0.3891    |
| O1 1                                   | 0.2871(8) | 1/4 | 0.3236(7) |
| O2 1                                   | 0.3742(7) | 1/4 | 0.0188(7) |
| O3 1                                   | 0.4822(6) | 1/4 | 0.7832(6) |
| O4 1                                   | 0.078(1)  | 1/4 | 0.0770(6) |

| $x = 1$ $^b$ SrYCeO$_4$ | Atom | Occupancy | $x$ | $y$ | $z$ |
|-------------------------|------|-----------|-----|-----|-----|
| Sr 1                    | 0.2509(3) | 1/4 | 0.6482(2) |
| Y1 1                    | 0.0746(2)  | 1/4 | 0.3880(2) |
| Y2 1                    | 0.5844(3)  | 1/4 | 0.6118(2) |
| Ce1 1                   | 0.0746    | 1/4 | 0.0746    |
| Ce2 1                   | 0.0746    | 1/4 | 0.0746    |
| O1 1                    | 0.278(2)   | 1/4 | 0.319(1)  |
| O2 1                    | 0.374(1)   | 1/4 | 0.012(1)  |
| O3 1                    | 0.487(1)   | 1/4 | 0.787(1)  |
| O4 1                    | 0.086(2)   | 1/4 | 0.079(1)  |

$^a$ All atoms are placed at general 4c positions. $^b$ At refinement of SrY$_2$O$_4$, isotropic atomic displacement parameters ($U_{iso}$) of four oxygen atoms were constrained to be equal. $^c$ Because of the disordering of Y and Ce atoms, the fractional coordinate and $U_{iso}$ were constrained to the same values, respectively. In order to refine the occupation ratio of Ce atoms, $U_{iso}$ parameters of Sr, Y and O atoms were fixed to the respective values of each atoms at non-doped SrY$_2$O$_4$. 

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**Fig. 2** Observed (red + symbols), calculated (solid line) and difference blue line patterns for the Rietveld refinement from the X-ray powder diffraction data of the synthesized SrY$_2$O$_4$ (a), SrY$_{1.8}$Ce$_{0.2}$O$_4$ (b) and SrYCeO$_4$ (c).
sites affects the Ce\(^{3+}\) occupancy. In fact, the occupancy ratio, Ce\(2/\text{Ce}1\), was 0.25 for SrY\(_{1.8}\text{Ce}0.2\)O\(_4\) (\(x = 0.2\)), while it was 0.56 for SrY\(_2\)Ce\(_x\)O\(_4\) (\(x = 1\)). These results indicate that the Ce\(^{3+}\) ions were preferentially located in the energetically favoured ideal octahedral Y(1) site when the Ce\(^{3+}\) concentration was low, and suggest that the distorted Y(2) site were also begun to be occupied when the Ce\(^{3+}\) concentration was increased and the solubility in the Y(1) sites were saturated.

Fig. 4 shows the FE-SEM images of the SrY\(_2\)Ce\(_x\)O\(_4\) (\(x = 1\)) sample at different magnifications. Since it was synthesized at a high temperature of 1300 °C, the primary particles melted to form large secondary particles.

**Reflectance spectra**

The UV-vis reflectance and absorption spectra of SrY\(_{2-x}\text{Ce}x\)O\(_4\) (0 ≤ \(x\) ≤ 1.2) are depicted in Fig. 5. The absorbance spectra were represented by the Kubelka–Munk function, \(f(R) = (1 - R)^2/2R\), where \(R\) is reflectance.\(^{18}\) The non-doped SrY\(_2\)O\(_4\) sample showed high reflectance in the visible light region of 400 to 750 nm. In the case of the Ce\(^{3+}\)-doped SrY\(_{2-x}\text{Ce}x\)O\(_4\) (0.2 ≤ \(x\) ≤ 1.2) samples, on the other hand, optical absorption were observed due to the O\(_{2p}\)-Ce\(_{4f}\) charge transfer transition at a wavelength of 380 nm or shorter as well as the 4f-5d allowed transition of Ce\(^{3+}\) in the wavelength range from violet to green (400–550 nm).\(^{28-30,39}\) As the concentration of Ce\(^{3+}\) increased, the absorption due to the 4f-5d transition appeared more intensely. In addition, the reflectance at 600 nm and longer wavelengths also decreased when the Ce\(^{3+}\) concentration became high.

These results are considered to be due to the existence of two non-equivalent octahedral Y sites of different coordination environments in the crystal structure of SrY\(_2\)O\(_4\). As mentioned above, Y(1) site is located in the ideal octahedral coordination environment and the other Y(2) site is significantly distorted,\(^{31}\) as illustrated in Fig. 3. The band structure models of the ideal Y(1) and the distorted Y(2) sites in the SrY\(_{2-x}\text{Ce}x\)O\(_4\) (0 ≤ \(x\) ≤ 1.2) samples are illustrated schematically in Fig. 6. The valence band (VB) and the conduction band (CB) consist of O\(_{2p}\) and Y\(_{3d}\) orbitals, respectively. When the Ce\(^{3+}\) ions are doped into the SrY\(_2\)O\(_4\) lattice, the 4f and 5d energy levels of Ce\(^{3+}\) are introduced between VB (O\(_{2p}\) orbital) and CB (Y\(_{3d}\) orbital). Since the crystal field energy around the Ce\(^{3+}\) ions in the distorted Y(2) site is stronger than that in the ideal Y(1) site, the 5d orbital energy
splitting of Ce\(^{3+}\) in the Y(2) site is also larger than that in the Y(1) site. As already discussed, the Ce\(^{3+}\) preferentially occupies the ideal Y(1) in the low Ce\(^{3+}\) concentration sample, and the Y(2) occupancy was increased with increasing the Ce\(^{3+}\) concentration. Accordingly, the optical absorption at 600 nm and longer wavelengths was observed in the samples with high Ce\(^{3+}\) concentration.

**Chromatic properties**

The chromatic parameters of the synthesized SrY\(_{2-x}\)Ce\(_x\)O\(_4\) (0 ≤ x ≤ 1.2) pigments are summarized in Table 4. The photographs of these pigments are also displayed in Fig. 7. The $L^*$ values increased as the amount of Ce\(^{3+}\) decreased. The $a^*$ and $b^*$ values increased in a positive direction. As already discussed above regarding the results in Fig. 3, these relationships can be attributed to the difference of coordination environment around the Ce\(^{3+}\) ions. When the Ce\(^{3+}\) concentration is relatively low, the Ce\(^{3+}\) ions are preferentially located in the ideal octahedral Y(1) site. Since the crystal field of Ce\(^{3+}\) in the Y(1) site is relative small, the 4f-5d allowed transition of Ce\(^{3+}\) in this site is observed at the wavelengths in the region of violet to blue green (400–550 nm). As a result, the samples are yellow, which is complementary colour of blue. On the other hand, the samples containing Ce\(^{3+}\) at high concentrations additionally absorbed light at wavelengths of 600 nm and above, corresponding to the 4f-5d allowed transition of Ce\(^{3+}\) in the distorted octahedral Y(2) site. Accordingly, the samples gradually became reddish with increasing the Ce\(^{3+}\) content. Among the SrY\(_{2-x}\)Ce\(_x\)O\(_4\) samples synthesized in this study, SrYCeO\(_4\) is the most reddish ($a^* = +21.8$).

**Thermal and chemical stability tests**

The thermal and chemical stabilities of the SrYCeO\(_4\) pigment were evaluated using the powder sample. To evaluate the thermal stability, this sample was heated in a mullite crucible at 300 °C and 500 °C for 3 h under an air atmosphere and cooled to room temperature. The acid/base resistance of the SrYCeO\(_4\) pigment was tested in 4% acetic acid and 4% ammonium bicarbonate solutions, and the pigment was dispersed into the acid/base solutions. After leaving them at room temperature for...
1 h, the sample was washed with deionized water and ethanol, and then dried at room temperature.

The colour of the samples after the thermal and chemical stability tests were evaluated using the colorimeter. The colour coordinate data are summarized in Table 5. Unfortunately, the heat resistance of this sample was low, and the colour degradation was observed after heating the present SrYCeO4 pigment at 300 °C and above in air. On the other hand, the SrYCeO4 pigment has chemical stability. The colour was almost unchanged after the leaching test in the acetic acid and ammonium bicarbonate solutions.

In order to investigate the reason for the color degradation after the heating in air, oxidation state of the cerium ions of the SrYCeO4 samples was identified by the XPS measurement before and after the heat resistance tests. The Ce (3d5/2) and Ce (3d3/2) XPS obtained from the SrYCeO4 sample before and after the heat resistance tests are shown in Fig. 8. In addition to the binding energy peaks for Ce3+ at 884.2 (V) and 902.4 (U) eV, four peaks corresponding to Ce4+ species on the surface of the SrYCeO4 samples was identified by the XPS measurement before and after the heat resistance tests. The Ce (3d5/2) and Ce (3d3/2) spin–orbit components. The intensities of two peaks assigned to Ce3+ decreased with increasing the calcination temperature, in comparison with those of the as-synthesized sample. Therefore, the colour degradation will be caused by the oxidation of Ce3+ to Ce4+.

Table 5 Colour coordinates of SrYCeO4 before and after thermal and chemical stability tests

| Pigment                  | L*  | a*  | b*  | C   | h°  |
|--------------------------|-----|-----|-----|-----|-----|
| As synthesized           | 49.1| +21.8| +42.2| 47.5| 62.7|
| 300 °C in air            | 94.5| −0.33| +3.12| 3.14| 96.0|
| 500 °C in air            | 95.4| −0.94| +3.41| 3.54| 105|
| 4% CH3COOH               | 49.3| +17.5| +41.1| 44.7| 66.9|
| 4% NH4HCO3               | 46.7| +18.7| +40.6| 44.7| 65.3|

Fig. 8 Ce (3d) XPS for SrYCeO4 samples before and after heat resistance test.

Conclusions

SrY2-xCe2O4 (0 ≤ x ≤ 1.2) were synthesized using a citrate sol-gel method as environmentally friendly inorganic reddish-brown pigments. The samples exhibited optical absorption due to the 4f–5d allowed transition of Ce3+ at wavelengths from 410 to 500 nm and at 600 nm and longer. The former is attributed to the 4f–5d transition of Ce3+ in the ideal octahedral Y(1) site, and the latter is due to that in the distorted octahedral Y(2) site. Since the Ce3+ ions were preferentially dissolved into the energetically favoured Y(1) site, the colour of the samples gradually changed from yellow to reddish brown with increasing the Ce3+ concentration. The most reddish colour was observed for SrYCeO4 (a* = +21.8). Since this compound is consisted with non-toxic elements, it is expected to be an environmentally friendly inorganic reddish-brown pigment.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number 15K05643. The authors thank Dr Hirokazu Izumi (Hyogo Prefectural Institute of Technology) for his assistance with X-ray photoelectron spectroscopy measurements.

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