Synthesis and characterisation of Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ ($0 \leq x \leq 0.50$) for blue-violet inorganic pigments

Takashi Tsukimori, Yusuke Shobu, Ryohei Oka and Toshiyuki Masui*

Bazn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ ($0 \leq x \leq 0.50$) solid solutions were synthesized as novel blue-violet inorganic pigments by a conventional solid-state reaction method. The crystal structure, optical properties, and colour of the pigments were characterized. All the pigments were obtained in a single-phase form. The pigments strongly absorbed visible light at wavelengths from 550 to 650 nm, corresponding to the range of green to orange light. This optical absorption was caused by the d–d transition of the tetrahedrally coordinated Co$^{2+}$ ($^4A_2(F) \rightarrow ^4T_1(P)$), which was the origin of the blue-violet colour of the pigments. The most intense colour was obtained for BaZn$_{1.85}$Co$_{0.15}$Si$_2$O$_7$, where $a^* = +52.2$ and $b^* = -65.5$ in the CIE (Commission Internationale de l’Eclairage) L*a*b* system. These absolute values were significantly larger than those of commercial violet pigments such as Co$_3$(PO$_4$)$_2$ ($a^* = +33$ and $b^* = -32$) and NH$_4$MnP$_2$O$_7$ ($a^* = +39$ and $b^* = -21$). Therefore, the BaZn$_{1.85}$Co$_{0.15}$Si$_2$O$_7$ pigment could be a novel blue-violet inorganic pigment.

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Ni$_2$Si$_2$O$_7$ (M = Zn or Mg) pigments have been ever reported, but they exhibit red and purplish red colours due to the d-d transition of the tetrahedral coordinated Ni$^{2+}$.$^{24}$ In this study, Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ x ≤ 0.50) pigments were synthesized by a conventional solid-state reaction method, and the colour properties of the pigments were investigated as novel blue-violet inorganic pigments.

**Experimental**

**Materials and methods**

The Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ x ≤ 0.50) pigments were synthesized by a conventional solid-state reaction method. BaCO$_3$ (Kishida Chemical, Japan), ZnO (Kishida Chemical, Japan), SiO$_2$ (Wako Pure Chemical, Japan) and Co$_3$O$_4$ (Wako Pure Chemical, Japan) were used as starting materials. The raw materials were mixed in a stoichiometric amount in an agate mortar. The mixture was calcined in an alumina boat at 1250°C for 6 h. The samples were ground in an agate mortar before characterisation.

**Characterisation**

The composition of the samples was confirmed by X-ray fluorescence spectroscopy (XRF; Rigaku, ZSX Primus). The crystal structures of the samples were identified by X-ray powder diffraction (XRD; Rigaku, Ultima IV) with Cu-Kα radiation (40 kV, 40 mA). The sampling width and the scan speed were 0.02° and 6.0 min$^{-1}$, respectively. The lattice parameters and volumes were calculated from the XRD peak angles, which were re

**Results and discussion**

**X-ray fluorescence analysis (XRF)**

The XRF analysis data of the samples were listed in Table 1. All compositions were almost in good agreement with those of the nominal stoichiometric ones.

**X-ray powder diffraction (XRD)**

Fig. 1 shows the XRD patterns of the Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ x ≤ 0.50) pigments. All samples were obtained in a single-phase form and the diffraction patterns were well indexed to that of the monoclinic BaZn$_2$Si$_2$O$_7$ structure whose space group was $C2/c$. This structure is different from that of orthorhombic BaCu$_2$Si$_2$O$_7$ (ref. 26) having a similar composition. The diffraction peaks about 54° shifted to higher angles with increasing the Co$^{2+}$ content. The lattice volumes of the Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ x ≤ 0.50) samples calculated from the diffraction peaks are

| Stoichiometric composition | Analytical composition |
|----------------------------|------------------------|
| BaZn$_{1.0}$Si$_2$O$_7$     | Ba$_{0.99}$Zn$_{0.99}$Si$_{2.02}$O$_{0.02}$ |
| Ba(Zn$_{0.95}$Co$_{0.05}$)$_2$Si$_2$O$_7$ | Ba$_{0.93}$Zn$_{0.93}$Co$_{0.04}$Si$_{2.11}$O$_{0.15}$ |
| Ba(Zn$_{0.90}$Co$_{0.10}$)$_2$Si$_2$O$_7$ | Ba$_{0.89}$Zn$_{0.89}$Co$_{0.11}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ | Ba$_{0.84}$Zn$_{0.84}$Co$_{0.13}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.80}$Co$_{0.20}$)$_2$Si$_2$O$_7$ | Ba$_{0.80}$Zn$_{0.80}$Co$_{0.21}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.75}$Co$_{0.25}$)$_2$Si$_2$O$_7$ | Ba$_{0.77}$Zn$_{0.77}$Co$_{0.21}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.70}$Co$_{0.30}$)$_2$Si$_2$O$_7$ | Ba$_{0.70}$Zn$_{0.70}$Co$_{0.29}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.65}$Co$_{0.35}$)$_2$Si$_2$O$_7$ | Ba$_{0.65}$Zn$_{0.65}$Co$_{0.34}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.60}$Co$_{0.40}$)$_2$Si$_2$O$_7$ | Ba$_{0.60}$Zn$_{0.60}$Co$_{0.35}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.55}$Co$_{0.45}$)$_2$Si$_2$O$_7$ | Ba$_{0.55}$Zn$_{0.55}$Co$_{0.36}$Si$_{2.16}$O$_{0.00}$ |
| Ba(Zn$_{0.50}$Co$_{0.50}$)$_2$Si$_2$O$_7$ | Ba$_{0.50}$Zn$_{0.50}$Co$_{0.37}$Si$_{2.16}$O$_{0.00}$ |
summarized in Table 2. The volume decreased with increasing the Co$^{2+}$ concentration, indicating that the Zn$^{2+}$ (ionic radius: 0.060 nm)$^{27}$ ions were partially substituted with the smaller Co$^{2+}$ (ionic radius: 0.058 nm)$^{27}$ ions and the solid solutions based on monoclinic BaZn$_2$Si$_2$O$_7$ were successfully synthesized in a single-phase form.

### Table 2 Lattice volumes of the Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ $x$ ≤ 0.50) pigments

| $x$  | Lattice volume/nm$^3$ |
|------|----------------------|
| 0    | 1.27603              |
| 0.05 | 1.27570              |
| 0.10 | 1.27559              |
| 0.15 | 1.27555              |
| 0.20 | 1.27497              |
| 0.25 | 1.27463              |
| 0.30 | 1.27449              |
| 0.35 | 1.27383              |
| 0.40 | 1.27370              |
| 0.45 | 1.27356              |
| 0.50 | 1.27330              |

Scanning electron microscopic (SEM) image and energy dispersive X-ray (EDX) analysis

Fig. 2 depicts the SEM image and particle distribution of the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ pigment. The average particle size calculated from 400 particles was about 13 μm. The EDX analysis result for the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ sample is shown in Fig. 3. It was confirmed that Ba, Zn, Si, Co and O were present and non-impurities were observed without Au (charge-up preventer). The X-ray dot mapping analysis results is depicted in Fig. 4, indicating that the component elements were uniformly distributed in the particle.

**X-ray photoelectron spectrum (XPS)**

The XPS of the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ pigment is shown in Fig. 5. This spectrum was deconvoluted into three components, considering the spin–orbit doublets. The intense peaks at 795.3 eV and 780.2 eV were attributed to the Ba$^{2+}$ 3d$^{3/2}$ and 3d$^{5/2}$ configurations, respectively.$^{28,29}$ Although the small peaks observed at 793.7 eV and 778.6 eV were assigned to the Co$^{3+}$ 2p$^{3/2}$ and 2p$^{1/2}$ lines, more intense peaks were also detected at 796.3 eV and 781.0 eV, corresponding to those of Co$^{2+}$. These results indicate that the dominant oxidation state of cobalt ions was divalent on the surface of the Ba(Zn$_{x}$Co$_{0.15}$)$_2$Si$_2$O$_7$ pigment. Furthermore, the d–d transition of the tetrahedral coordinated Co$^{3+}$ ions was appeared around 9000 cm$^{-1}$ (1111 nm).$^{32}$ Therefore, the Co$^{3+}$ ions do not affect the colour of the present Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0.05 ≤ $x$ ≤ 0.50) pigments.

**Reflectance spectra**

Fig. 6 depicts the UV-Vis diffuse reflectance spectra for the Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0 ≤ $x$ ≤ 0.50) pigments. High reflectance was observed in the visible light region for the Co$^{2+}$-free BaZn$_2$Si$_2$O$_7$ ($x = 0$) sample. On the other hand, strong absorption bands originated by the d–d transition of tetrahedral coordinated Co$^{3+}$ (ref. 8, 33 and 34) were observed in the Ba(Zn$_{1-x}$Co$_x$)$_2$Si$_2$O$_7$ (0.05 ≤ $x$ ≤ 0.50) pigments from 550 to 650 nm corresponding to the green-orange lights. The Co$^{3+}$ ion has the d$^7$ electron configuration and the energy level structure of the Co$^{2+}$ ion in a tetrahedral site is similar to that of d$^3$ ion in an octahedral site.$^{35}$ According to the Tanabe–Sugano diagram, the bands from 550 to 650 nm are assigned to the $^4$A$_2$(F) → $^4$T$_1$(P) transition of the tetrahedral coordinated Co$^{2+}$.$^{31–36}$

![Fig. 2 SEM image (a) and particle distribution (b) of the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ pigment.](image1)

![Fig. 3 The EDS analysis for Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$.](image2)
Chromatic properties

The $L^*a^*b^*Ch^*$ colour coordinate data for the Ba($\text{Zn}_{1-x}\text{Co}_x$)$_2\text{Si}_2\text{O}_7$ pigments are summarized in Table 3. They were compared using powder samples. It is obvious that the $a^*$ and $b^*$ values became significantly positive and negative, respectively, by the introduction of Co$^{2+}$ in the host BaZn$_2$Si$_2$O$_7$ lattice. As mentioned in the previous section, the Ba($\text{Zn}_{1-x}\text{Co}_x$)$_2\text{Si}_2\text{O}_7$ pigments absorbed the green-orange lights but reflected the complementary blue and red lights. This is the reason for that positive $a^*$ and negative $b^*$ values were obtained in these pigments. The photographs of the Ba($\text{Zn}_{1-x}\text{Co}_x$)$_2\text{Si}_2\text{O}_7$ ($0 \leq x \leq 0.50$) samples are shown in Fig. 7. The colour of the Ba($\text{Zn}_{1-x}\text{Co}_x$)$_2\text{Si}_2\text{O}_7$ ($0 \leq x \leq 0.50$) pigments gradually changed from white to dark blue-violet as the Co$^{2+}$ concentration increased. Among the samples synthesized in this study, the largest absolute values in the colour coordinate data were obtained for Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ ($a^* = +52.2$ and $b^* = -65.5$).

They were compared with those of the commercially available Co$_3$(PO$_4$)$_2$ and NH$_4$MnP$_2$O$_7$ pigments in Table 4. It is notable that the absolute values of $a^*$ and $b^*$ for the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ were significantly larger than those for the commercial violet pigments.

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Fig. 4 The X-ray dot mapping analysis of the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$.

Fig. 5 XPS of Co 2p and Ba 3d on the surface of the Ba(Zn$_{0.85}$Co$_{0.15}$)$_2$Si$_2$O$_7$ pigment.

Fig. 6 UV-Vis reflectance spectra of the Ba($\text{Zn}_{1-x}\text{Co}_x$)$_2\text{Si}_2\text{O}_7$ ($0 \leq x \leq 0.50$) pigments.
at room temperature. The colour of the pigment was also evaluated using a powder sample. The pigment was soaked into 4% acetic acid and 4% ammonium bicarbonate. After leaving them at room temperature for 2 h, the pigments were washed with deionized water and ethanol, and then dried at room temperature. The colour of the pigment after the leaching test was evaluated using the calorimeter. As seen in Table 5, the colour of the present Ba(Zn0.85Co0.15)2Si2O7 pigment was almost unchanged.

Table 3 The L*a*b*Ch+ colour coordinates of the Ba(Zn1−xCox)2Si2O7 (0 ≤ x ≤ 0.50) pigments

| x   | L*   | a*   | b*   | C    | h°   |
|-----|------|------|------|------|------|
| 0   | 93.7 | −0.01| +0.20| 0.20 | 92.9 |
| 0.05| 43.8 | +27.9| −46.6| 54.3 | 300.9|
| 0.10| 30.1 | +39.8| −54.8| 67.7 | 306.0|
| 0.15| 28.6 | +52.2| −65.5| 83.8 | 308.6|
| 0.20| 25.9 | +44.9| −57.8| 76.4 | 307.8|
| 0.25| 21.8 | +49.9| −59.8| 77.9 | 309.8|
| 0.30| 25.0 | +33.3| −45.4| 56.3 | 306.3|
| 0.35| 22.8 | +27.4| −38.0| 46.8 | 305.8|
| 0.40| 21.0 | +35.9| −45.3| 58.3 | 308.0|
| 0.45| 20.2 | +33.4| −43.3| 54.6 | 307.6|
| 0.50| 20.8 | +30.4| −40.5| 50.6 | 306.9|

Chemical stability tests

The chemical stability of the Ba(Zn0.85Co0.15)2Si2O7 pigment was also evaluated using a powder sample. The pigment was soaked into 4% acetic acid and 4% ammonium bicarbonate. After leaving them at room temperature for 2 h, the pigments were washed with deionized water and ethanol, and then dried at room temperature. The colour of the pigment after the leaching test was evaluated using the calorimeter. As seen in Table 5, the colour of the present Ba(Zn0.85Co0.15)2Si2O7 pigment was almost unchanged.

Table 4 The L*a*b*Ch+ colour coordinates of the Ba(Zn0.85Co0.15)2Si2O7 pigment and commercial violet pigments

| Samples                  | L*   | a*    | b*    | C    | h°   |
|--------------------------|------|-------|-------|------|------|
| Ba(Zn0.85Co0.15)2Si2O7   | 28.6 | +52.2 | −65.5 | 83.8 | 308.6|
| Co3(PO4)2                | 46   | +33   | −32   | 44.3 | 315.9|
| NH4MnP2O7                 | 31   | +39   | −21   | 46.0 | 331.7|

* Cited from ref. 20.

Table 5 The L*a*b*Ch+ colour coordinates of the Ba(Zn0.85Co0.15)2Si2O7 pigment before and after the acid and base resistance tests

| Pigment                  | L*   | a*    | b*    | C    | h°   |
|--------------------------|------|-------|-------|------|------|
| Non-treatment            | 28.6 | +52.2 | −65.5 | 83.8 | 308.6|
| 4% CH3COOH               | 28.0 | +57.0 | −69.4 | 89.8 | 309.4|
| 4% NH4HCO3               | 25.7 | +56.2 | −67.8 | 88.1 | 309.7|

Conclusions

Ba(Zn1−xCox)2Si2O7 (0 ≤ x ≤ 0.50) solid solutions were successfully synthesized as novel blue-violet inorganic pigments. The samples strongly absorbed the visible light from 550 to 650 nm (green to orange), which was originated by the d–d transition of tetrahedrally coordinated Co2+. Ba(Zn0.85Co0.15)2Si2O7 showed the most intense colour among the samples, and the L*a*b*Ch+ parameters were L* = 28.6, a* = +52.2, b* = −65.5, C = 66.3, and h° = 308.6. The absolute values of a* and b* of Ba(Zn0.85Co0.15)2Si2O7 were significantly larger than those of the commercial Co3(PO4)2 (a* = +33 and b* = −32) and NH4MnP2O7 (a* = +39 and b* = −21) pigments. Furthermore, the Ba(Zn0.85Co0.15)2Si2O7 pigment has excellent chemical resistance and thermal stability. These results indicate that Ba(Zn0.85Co0.15)2Si2O7 could serve as an effective alternative to the conventional blue-violet inorganic pigments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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