Synthesis of new Cr-doped CaTiO₃ yellow pigments by a simple solvothermal method

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Cr-doped calcium titanate (CaTiO₃) pigments with prism-like shape were synthesized by a simple solvothermal process without any surfactants. The colouring mechanism and performance of Cr-doped CaTiO₃ yellow pigment samples were investigated by X-ray diffraction, diffuse reflection spectroscopy, field scanning electron microscopy and colorimeter. When Cr-doping concentrations were 0.01–0.05% (mole fraction, the same below), solid solution formed so that the yellow pigments would have a CaTiO₃ phase composition. The intensity of the yellow colour in the pigment samples was related to the presence of Cr ions. The optimum yellow pigment was achieved when the Cr-doping concentration was 0.03% mol. At a high temperature of 1280°C, Cr-doped CaTiO₃ yellow sample provided a stronger and more intense colour as Cr ions dissolved into the stable CaTiO₃ structure. This solvothermal preparation method provides a simpler way to synthesize a more colourful ceramic pigment that can be applied in ceramic decoration or inkjet printers.

Key-words : Cr-doped CaTiO₃, Yellow pigment, Template free, Solvothermal method

1. Introduction

Yellow pigment as one of the Inkjet printing inks has been widely used for the Cyan-Magenta-Yellow-black (CMYK) printing system in industrial ceramic decoration.¹ Although new environmental friendly yellow inorganic transition metal oxides pigments like SnO₂ are obtained,²,³ this kind of pigment is not suitable for high temperature glaze (>1250°C) as SnO₂ in the pigment would react with other oxides in the glaze. Nowadays, praseodymium zinc yellow, vanadium-zirconia yellow, etc. are used as the deep yellow hue in ceramic pigments for high temperature glaze (>1250°C).⁴ However, these high-temperature yellow ceramic pigments are very expensive for the industrial ceramic decoration.

Pervoskite structure is used widely as the host crystal in fields and catalyst control technique area.¹,³ CaTiO₃ belongs to the basic family of pervoskite due to the ideal cubic structure. It is commonly well-known that the size and morphology of materials would affect their physical and chemical properties greatly. As an eco-friendly aqueous process, solvothermal methods are attractive in fabricating CaTiO₃ with well-controlled stoichiometry, precisely-tailored morphology and high crystallinity.⁵ Due to its wide application in the biomedica, electrical fields and catalyst control technique area,¹,³ CaTiO₃ has been one of the most well-known and popular materials. Compared to the former, there are few reports for colouring properties of CaTiO₃.

In this paper, CaTiO₃ pigment with prism-like structure was prepared by a simple solvothermal method. The aim of this work was to assess both colouring performance and potential of Cr-doped CaTiO₃ pigment in high-temperature ceramic glaze decoration. This method investigated the microstructure of CaTiO₃ pigment in determining its coloration and high temperature colour stability. The pigments were characterized by X-ray diffraction (XRD), scanning electron microscopy (FESEM), UV–Vis absorption, laser scattering particle size distribution analyzer and colorimeter.

2. Experimental procedure

2.1 Synthesis

All reagents were commercially available and used directly without further purification. The CaTiO₃ crystals were synthesized in an aqueous medium via a hydrothermal route. In a typical synthesis process, firstly, mixing 0.01 mol Ti(Oi-C₄H₉)₄ (TBOT) with water and ethanol whose molar ratio is 1:1 inside the autoclave, followed by adding 0.01 mol CaCl₂·5H₂O and chronic chloride hydrate with different molar contents (0, 0.01, 0.03, 0.05, 0.07 and 0.1% mol respectively) into the mixture. Secondly, the mixture is vigorously stirred at room temperature for 5 min, then added 3 M of NaOH to adjust the pH to be 13. Thirdly, the autoclave is sealed and kept the temperature at 180°C for 36 h, and then allowed the mixture to cool down to room temperature naturally. Afterward, the final products were centrifuged, and washed with deionise water and absolute ethanol for several times before allowing them to dry in hot air at 80°C for 15 h. The Cr-doped CaTiO₃ pigment was prepared in the same way.

The Cr-doped CaTiO₃ pigment (3 g) was mixed with the transparent glaze (10 g, with the melting temperature of 1280–1300°C) and water (20 g). The obtained suspension was dipped on the porcelain and the porcelain was calcined at 1280°C for 10 min.

2.2 Characterization

The morphologies of the powders were investigated by field emission scanning electron microscopy (FESEM, KYKY-1000B,
concentration exceeds beyond 0.07 when the Cr-doping concentrations increase. When the Cr-doping phase appears along with the major phase of CaTiO$_3$ (See Fig. 2).

The formation of the chromium compound may be due to the solid-solution formation. Moreover, the Ti$_8$O$_{15}$ phases decrease with the increase of the Cr-doping concentration. The red shift of the as-prepared pigment samples could be indicative of the lattice constant change, which results in lattice distortion. These results are in accordance with those of XRD patterns (See Table 1). Therefore, the absorption edges around 460 nm of the pigment samples display red shift with the increase of the Cr-doping concentration. The red shift occurs with the increase of the Cr-doping concentration. Owing to the bigger particle size of Cr ions as compared to Ti ions, the absorption bands shift to the blue light range where is longer wavelength and lower energy. The absorption band absorbs the blue light and reflects yellow light.

Figure 3 shows the UV–visible absorption curves of Cr-doped CaTiO$_3$ pigment samples with various Cr-doping concentrations. With the increase of the Cr-doping concentration, the absorption edges of the samples display red shift. Theoretically, the red shift occurs with the increase of the Cr-doping concentration. The red shift of the as-prepared pigment samples could be indicative of the lattice constant change, which results in lattice distortion. These results are in accordance with those of XRD patterns (See Table 1). Therefore, the absorption edges around 460 nm of the pigment samples display red shift with the increase of the Cr-

![Fig. 2. XRD patterns of the pigment samples with various Cr-doping concentrations (mol): (a) 0, (b) 0.01%, (c) 0.03%, (d) 0.05%, (e) 0.07%.

![Fig. 3. UV–visible absorption curves of un-doped CaTiO$_3$ sample (a) and CaTiO$_3$ yellow pigment samples with various Cr-doping concentrations (mol): (b) 0.01%, (c) 0.03%, (d) 0.05%.

Table 1. Colour properties of the pigment samples with various Cr-doping concentrations

| Cr-doping concentration (% mol) | L$^*$ | a$^*$ | b$^*$ | Lattice constant/A | Cell volume (Å$^3$) |
|-------------------------------|-------|-------|-------|-------------------|-------------------|
| 0                             | 0     | 0     | 0     | 10.739(3)         | 890.997           |
| 0.01                         | 88.10 | 2.86  | 15.67 | 10.74(4)         | 891.35            |
| 0.03                         | 80.91 | 2.82  | 18.26 | 10.752(6)        | 892.56            |
| 0.05                         | 79.68 | 3.76  | 18.52 | 10.753(2)        | 892.62            |

The lattice constant and cell volume are solved by direct methods and Fourier synthesis with the program SHELXS-97.  

3. Results and discussion

We have systematically investigated the system with various Cr-doping concentrations while keeping the other reaction conditions unchanged. The expected phase composition for yellow pigment is CaTiO$_3$ that prepared by the solvothermal method. Figure 1 shows photographs of the pigments with various Cr-doping concentrations. It is obvious that the yellow tone of the pigments is more intense with the increasing of the Cr-doping concentration, and the most intense coloration is provided by the pigment with 0.03% mol Cr-doping concentration. With further increase in Cr-doping concentration, the pigment appears green, which is due to the green colour of Cr$^{3+}$ ions.

Figure 2 shows the XRD patterns of the pigment samples with various Cr-doping concentrations. When Cr-doping concentration is 0 mol, the sample is CaTiO$_3$ (JCPDS card 09-3605) phase and a little of Ti$_8$O$_{15}$ (JCPDS card 11-0473) phase. As the amount of chromium ions diffusing into the CaTiO$_3$ structure increases, there is a slight shift of the peak position towards lower angles (Fig. 2). This behaviour suggests that Cr$^{3+}$ dissolved into CaTiO$_3$ structure produces internal strain, because Cr$^{3+}$ (0.615 Å) ions have bigger ionic radii as compared to Ti$^{4+}$ (0.605 Å) ions. As a result, the lattice parameter increases which further confirms the solid-solution formation. Moreover, the Ti$_8$O$_{15}$ phases decrease when the Cr-doping concentrations increase. When the Cr-doping concentration exceeds beyond 0.07% mol, chromium compound phase appears along with the major phase of CaTiO$_3$ (See Fig. 2). The formation of the chromium compound may be due to the low solubility of Cr in CaTiO$_3$ at higher concentrations of Cr ions. The crystal lattice constant of the synthesized CaTiO$_3$ with various Cr-doping concentrations are summarized in Table 1. As shown in Table 1, the pigment with 0.03% mol Cr-doping concentration shows the brightest yellow color, which is in accordance with Fig. 1. Further increasing the Cr-doping concentration till 0.05% mol would lead to a considerable change in colour tones, however, the sample is still yellow colour. The values of the lattice constant and cell volume increase with the increase of the Cr-doping concentration. Owing to the bigger particle size of Cr ions as compared to Ti ions, the absorption bands shift to the blue light range where is longer wavelength and lower energy. The absorption band absorbs the blue light and reflects yellow light.

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doping concentration. All Cr-doped pigment samples absorb blue light around 460 nm efficiently which is yellow complementary colour, and thus the pigment samples show yellow colour (Fig. 1). Moreover, the Cr-doped CaTiO₃ yellow pigment has a full absorption in the range of visible light wavelengths, while the commercial yellow pigment has a less absorption ability in red light area. The doping agents such as Cr ions extend the optical absorption spectrum of the CaTiO₃ to the visible light range by allowing d orbital electrons to absorb energy to jump to the conduction band. In particular, chromium ions, substituting with Ti⁺⁺ ions in the CaTiO₃ lattice, have showed a much better performance so far.⁹,¹⁰ As noted above, the colouring mechanism of Cr-doped CaTiO₃ yellow pigment may be attributed to the strong absorption of blue light around 460 nm and reflects yellow light (Figs. 1 and 3). The absorption band around 460 nm can be assigned to the d₂→tt₁₄ transition of chromium (III) ions in the six-coordinate geometry.¹¹,¹² Replacing some of the Ti cations with Cr ions imposes lattice strain or distortion in the lattice (Table 1), which affects the colour of the Cr-doped CaTiO₃ ceramic pigment.

The particle size of the pigment is one of the key to the colour pigmentation. The pigment with small particle size has large surface area, which leads to high surface coverage, high number of reflectance points, and thus more scattering. The particle size distribution of the typical pigment with various Cr-doping concentrations was investigated in water as the dispersion. Table 2 shows the mean value of particle size distribution D50, D10, and D90 of the pigment with various Cr-doping concentrations. Increasing Cr-doping concentration results in a decrease in D50 value. The application of the pigments into glaze requires D50 values that is approximately 8–11 μm. All pigments match the range of mean particle size distribution where pigments can be applied into glaze.

The composition of 0.03 mol Cr-doped CaTiO₃ was chosen to analyze the microstructure of the pigment. Figure 4 shows FESEM images of typical pigment samples with 0.03 mol Cr-doping concentration. It can be seen that pigment sample is composed of the rectangular prism shaped structure with even size of less than 5 μm.

The colour of the glazed sample after firing depends on the variety of pigments and glaze formulation.¹⁴,¹⁵ Table 3 presents CIE Lab values of the colour glazes with 5 wt% of the commercial pigments and as-prepared Cr-doped CaTiO₃ pigments.

Table 2. The particle size distribution of the pigment samples with various Cr-doping concentrations

| Cr-doping concentration (% mol) | The particle size of CaTiO₃ pigment samples | D10/μm | D50/μm | D90/μm |
|--------------------------------|-------------------------------------------|--------|--------|--------|
| 0                              |                                           | 0.349  | 8.065  | 20.48  |
| 0.01                           |                                           | 0.334  | 7.103  | 18.53  |
| 0.03                           |                                           | 0.204  | 1.311  | 8.008  |
| 0.05                           |                                           | 0.203  | 1.289  | 4.517  |
| 0.07                           |                                           | 0.200  | 1.159  | 3.892  |

Table 3. Processing condition and CIE Lab colorimetric parameters of conventional pigment and as-prepared pigment dispersed in glazes

| Pigment                          | Pigment contents dispersed in glazes (% wt%) | Firing temperature (°C) | CIE Lab colorimetric parameters of the glaze |
|----------------------------------|---------------------------------------------|-------------------------|---------------------------------------------|
| Commercial zirconium yellow pigment | 5                                           | 1280                    | L* = 66.2, a* = 5.42, b* = 26.6             |
| The as-prepared yellow pigment    | 5                                           | 1280                    | L* = 66.14, a* = 5.62, b* = 27.8            |

Observing the colorimetric parameters (Table 3), the as-prepared 0.03% mol Cr-doped CaTiO₃ pigments show excellent yellow shades in transparent glaze after being fired at 1280°C (Fig. 5). The CIE coordination of the glaze is \( L^* = 66.14, a^* = 5.62, b^* = 27.87 \). It can be found that the deeper yellow color component \((b^* ≈ 40)\) is achieved with the 0.03% mol Cr-doped CaTiO₃ crystal structure (1280°C) in which the occurrence of \( Cr^{2+} \) is able to shift the band energy (Fig. 3). Cr-doped CaTiO₃ pigment sample gives rise in red component \((a^* ≈ 5.62)\), which is due to the change in lattice constants or lattice distortion resulting in provoking the absorption of blue light (Table 1). In any case, even though some color loss may occur due to glassy coatings, the chrome values \((i.e. c^* = a^* + b^*)\) are comparable in the glazes. Moreover, the commercial zirconium pigment, which is similar with the Cr-doped CaTiO₃ pigment, is also lost at 1280°C \((b^* ≈ 26.6, a^* ≈ 5.42)\) due to some reaction with glassy coatings. The results indicate that Cr-doped CaTiO₃ structure is stable at high temperature of 1280°C due to Cr dissolved into CaTiO₃ structure by the above procedure, and thus exhibits better thermal and chemical stability. It indicates Cr-doped CaTiO₃ is applicable as the high-temperature pigments in ceramic industry. Colorimeter data of Cr-doped CaTiO₃ ceramic pigment system also shows that this yellow pigment is suitable for ceramic applications.

4. Conclusion

In summary, Cr-doped CaTiO₃ yellow pigment was synthesized by a simple solvothermal process without any surfactants or template. Yellow pigment has CaTiO₃ phase composition. The applicable concentration range of the Cr-doping ions for yellow pigment (a) and commercial zirconium pigment (b).

Fig. 5. Photos of ceramic samples above a sheet of paper showing the yellow colour at 1280°C for the glazes added yellow pigment with 0.03% mol Cr-doped CaTiO₃ in the study (a) and commercial zirconium pigment (b).
pigment samples was 0.01–0.05 mol. The pigments presented good dispersion and could be dispersed directly in the glaze without further modification. The obtained yellow glazes has the L*, a* and b* value of 77.8, 11.3 and 39.6, respectively, even after being fired at 1280°C, which indicated the pigment is stable due to the formation of the solid solution. Cr-doped CaTiO3 yellow pigment could be a good candidate for ceramic tiles or inkjet printers. In addition, the solvothermal method provides a way to produce more colourful ceramic pigment.

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Reference
1) G. Buxbaum, Industrial inorganic pigments. 2nd ed. Wiley-VCH, Germany (1997) pp. 23–28.
2) V. S. Vishnu, S. Jose and M. L. P. Reddy, J. Am. Ceram. Soc., 94, 997–1001 (2011).
3) V. S. Vishnu, G. George, V. Diva and M. L. P. Reddy, Dyes Pigm., 82, 53–57 (2009).
4) E. Kato and H. Takashima, Rep. Gov’t. Res. Inst. Ceram. Kyoto, 4, 147–150 (1956).
5) J. Twu and P. K. Gallagher, Florida, CRC Press, New York (1992) pp. 5–76.
6) W. X. Dong, G. Zhao, B. Song, G. Xu, J. Zhou and G. Han, CrystEngComm, 14, 6990–6997 (2012).
7) N. Sayad, A. Saadi, S. Nemouchi, A. T. Benziada and C. Rabia, Stud. Surf. Sci. Catal., 175, 377–380 (2010).
8) M. F. Zhou, T. Bak, J. Nowotny, M. Rekas, C. C. Sorrell and E. R. Vance, J. Mater. Sci.: Mater. Electron., 13, 697–704 (2002).
9) L. Petra, T. Miroslav, L. Jana and J. Trojan, Dyes Pigm., 96, 264–268 (2013).
10) I. Robert and L. Radu, Dyes Pigm., 105, 152–156 (2014).
11) L. Li, Z. F. Yan, G. Q. Lu and Z. H. Zhu, J. Phys. Chem. B, 110, 178–183 (2006).
12) M. Kato, H. Unuma and M. Takahashi, J. Ceram. Soc. Japan, 108, 478–481 (2000).
13) S. T. Liang, H. L. Zhang, M. T. Luo, K. J. Luo, P. Li, H. B. Xu and Y. Zhang, Ceram. Int., 40, 4367–4373 (2014).
14) S. K. Biswas, D. Dhak, A. Pathak and P. Pramanik, Mater. Res. Bull., 43, 665–675 (2008).
15) S. Selvam, B. Rizwan, J. S. Kalarical, N. S. Sriman and U. N. Balachandran, Dyes Pigm., 94, 548–552 (2012).