

# Synthesis and near-infrared reflection performance of (Cr,V)-ZrSiO\_4 jewel green pigments

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# Abstract

Novel (Cr,V)-ZrSiO<sub>4</sub> jewel green pigments were synthesized by in situ mineralization at 900 °C. The effects of Cr/Si molar ratio were investigated via DTA-TG, XRD, FE-SEM, TEM, UV-Vis-NIR, colorimeter and etc. The obtained results referred that the colour of pigment exhibits blue to jewel green, and then to dark green as the Cr/Si molar ratio increases from 0 to 0.4. When the Cr/Si molar ratio is 0.2, the (Cr,V)-ZrSiO<sub>4</sub> pigment exhibits a jewel green hue  $(L^* = 56.69, a^* = -18.52, b^* = -9.28)$ , showing good rendering performance. In addition, the obtained pigment shows good thermal stability in the base glaze synthesized at 1200 °C and near-infrared reflection performance. The results of this study show great potential for using the pigments for heat insulation.

Keywords: pigments, zircon base, Cr-V co-doping, structure, optical properties, jewel green

# I. Introduction

Inorganic pigments have the advantages of high temperature resistance, anti-weathering, strong coverage and excellent solvent resistance. Therefore, the pigments play a pivotal role in ceramic industry [1–3]. According to the difference of crystal mineral structure types, the ceramic pigments can be divided into corundum-type, rutile-type, fluorite-type, spinel based and zircon (ZrSiO<sub>4</sub>) based [4– 8]. At present, zircon based pigments are the most widely used among ceramic pigments. Zircon based ceramic pigments contain almost all colour types and possess not only good rendering performance, but also have excellent high temperature stability, indicating the widespread application [9–12]. These properties are mainly due to the physical and chemical characteristics of zircon matrix, such as high melting point (2500 °C), low thermal

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conductivity, small expansion coefficient, strong corrosion resistance to molten glasses and acidic reagents, etc. [13,14]. The green zircon based pigments have received increasing attentions over recent years. Yang *et al.* [10] successfully synthesized green submicro-Cr-ZrSiO<sub>4</sub> ceramic pigments using 1 wt.% Li<sub>2</sub>CO<sub>3</sub> as mineralizer by solid-state method at 900 °C. The pigment shows a green hue ( $a^* = -10.13$ ), indicating that the Cr ions enter the zircon lattice. Ocana *et al.* [11] used NaF as the mineralizer to synthesize Cr-doped zircon pigments at 1100 °C by aerosol hydrolysis. Naga *et al.* [12] prepared Cr-ZrSiO<sub>4</sub> pigment using CaF<sub>2</sub>, LiF and NaF as mineralizers by reacting around 1200 °C. However, extremely high temperature leads to an increase in energy consumption, making it difficult for large-scale industrial production.

Nowadays, with the improvement of quality of life, people not only put forward colour requirements for pigments, but also hope to seek functional breakthroughs [15,16]. Studies have shown that the radiant energy of the sun is mainly concentrated in the visible and nearinfrared regions. By developing pigments with infrared

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reflection function and adding them to the coating system, relevant products with reflection and heat insulation function can be prepared. These products with excellent heat insulation function can be applied to buildings, roof surfaces and car shell coatings, ships and storage tanks [17,18]. Chromium doped pigments have some near-infrared properties [19,20]. However, there are few studies on the near-infrared reflection properties. In addition, most of the green ceramic pigments are coloured by chromium and the hue of pigments is relatively monotonous. Jewel green is a symbol of nobility, and it is popular with people. The jewel green pigment becomes main stream for its soft and bright colour, velvety texture. The Cr-V co-doping reduces the synthesis temperature while obtaining pigment with good rendering performance that also possesses near-infrared reflection performance. The use of vanadium is not only as a valuable colourant for the colouring but also a mineralizer to promote the crystal growth of zircon. Based on the previous research work [9], V-ZrSiO<sub>4</sub> ceramic pigment with good performance can be obtained with the additive content of  $Na_3VO_4$  of 10 mol%. In this work, we report a novel (Cr,V)-ZrSiO<sub>4</sub> jewel green pigment with nearinfrared reflection performance. The effect of Cr/Si molar ratio on the pigment performance was investigated.

#### **II.** Experimental details

#### 2.1. Preparation method

Analytical grade ZrOCl<sub>2</sub> · 8 H<sub>2</sub>O (Shanghai Aladdin Co. Ltd.) and Na<sub>2</sub>SiO<sub>3</sub> · 9 H<sub>2</sub>O (Shanghai Aladdin Co. Ltd.) were used as starting materials directly without further refinement. Na<sub>3</sub>VO<sub>4</sub> (Sinopharm Chemical Reagent Co. Ltd.) and Cr<sub>2</sub>O<sub>3</sub> (Sinopharm Chemical Reagent Co. Ltd.) were used without purification. In a typical process for the pigments synthesis, 10 mmol  $ZrOCl_2 \cdot 8H_2O$ , 10 mmol  $Na_2SiO_3 \cdot 9H_2O$ , 1 mmol Na<sub>3</sub>VO<sub>4</sub> and  $x \mod \%$  Cr (x = 0, 2.5, 5, 10, 20 and 40, 2-fold isometric interval for doping samples) were mixed and homogeneously ground in an agate mortar for 15 min. In the mechanical grinding process, the solid reaction between  $ZrOCl_2 \cdot 8H_2O$  and  $Na_2SiO_2 \cdot 9H_2O$ takes place. Then the mixture was transferred into a corundum crucible with a lid and calcined at desired temperature of 900 °C for 2h. After natural convection inside the furnace for cooling, the final products were obtained by washing with deionized water for three times, filtering and drying at 70 °C for 6 h.

The ceramic body and glaze were supplied by Peiyintang Ceramic Glaze Shop in Jingdezhen, China. The glazing process was performed by mixing the synthesized pigments with a transparent glaze (5/95 wt.% respectively), followed by calcination in air at 1200 °C for 30 min.

#### 2.2. Characterization

The crystalline phases were identified by X-ray diffraction analysis (XRD, D8 Advance, Bruker, Ger-

many) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) and the experimental data were collected in the  $2\theta = 10-70^{\circ}$  with step width and counting time of 0.02° and 0.2 s, respectively. The crystal structure of the sample was observed by field-emission scanning electron microscopy (FE-SEM, SU-8010, JEOL, Japan) and transmission electron microscope (TEM, JEM-2010, JEOL, Japan). The particle size and distribution range of the powders were characterized by laser particle size analyser (Mastersizer 3000, Malvern, UK), and the particle size distribution curve was given according to the results. The reflectance of the samples of visible and near-infrared light was characterized by UV-Vis-NIR spectrophotometer (PerkinElmer, Lambda 950). The colorimetric  $L^*a^*b^*$  parameters of the pigments and ceramic products were tested by an automatic WSD-3C whiteness meter (produced by Beijing Kangguang Instrument Co. Ltd.). In this system,  $L^*$  is the colour lightness (from black  $L^* = 0$  to white  $L^* = 100$ ,  $a^*$  is the green  $(-a^*)/\text{red}$  $(+a^*)$  axis, and  $b^*$  is the blue  $(-b^*)$ /yellow  $(+b^*)$  axis.

#### **III.** Results and discussion

#### 3.1. Structure and optical properties

Figure 1a shows the DTA-TG curves of the mixture with a Cr/Si molar ratio of 0.2. There is an obvious endothermic peak located at 119.8 °C accompanied by 11.72% weight loss in the range of room temperature to 500 °C, which is attributed to the evaporation of crystalline water. In the DTA curve, it can be observed that the other two sharp endothermic peaks are located at 794.6 °C and 1145.0 °C. The former endothermic peak is assigned to the melting of NaCl molten salt, while the latter is due to the volatilization of the molten salt [21]. The weight loss in the second stage on the TG curve is 29.02%.

Figure 1b shows XRD patterns of the samples with Cr/Si molar ratio of 0.2 at different temperatures. It can be seen that the main crystal phase of the samples at different temperatures is zircon phase (JCPDS No. 06-0266). The diffraction peaks intensities of the samples increase with the heat treatment temperature increasing, indicating the improvement of the crystallinity. Further increasing the temperature up to 950 °C resulted in little change in diffraction peak intensity. Besides, it can be found from the DTA-TG curve that the initial temperature of *in situ* molten salt volatilization is approximately 930 °C. The molten salt volatilizes too quickly when the firing temperature increases to 950 °C, which is not conducive to the growth of grains in the stable liquid phase. Consequently, the optimum heat treatment temperature is 900 °C.

Figure 2 shows the XRD patterns of the samples prepared with different Cr/Si molar ratios, i.e. 0.025, 0.05, 0.1, 0.2 and 0.4. For the sake of comparison, XRD pattern of the sample without Cr is also given in Fig. 2. As it can be seen, the primary crystalline phase of the samples is zircon phase (JCPDS No. 06-0266). The intensities of



Figure 1. (a) DTA-TG curves of mixture; (b) XRD patterns of sample at different temperatures



Figure 2. XRD patterns of samples with different Cr/Si molar ratios

diffraction peaks of zircon phase (JCPDS No. 06-0266) in the samples with Cr-V co-doping are significantly higher than that of the sample without Cr. The undesired  $Cr_2O_3$  heterophase can be observed in the sample with the Cr/Si molar ratio of 0.4. These results indicate that an appropriate amount of Cr-V co-doping can effectively promote the growth and development of  $ZrSiO_4$ crystal, while the excessive Cr-doping easily cause heterophase appearance and affect the synthesis of  $ZrSiO_4$ . Further, according to the ionic size factor affecting the solid solution type, the size conditions for forming the solid solution are shown in Eqs. 1 and 2:

Continuous solid solution 
$$\left| \frac{r_1 - r_2}{r_1} < 15\% \right|$$
 (1)

Finite solid solution 
$$\left| 15\% < \frac{r_1 - r_2}{r_1} < 30\% \right|$$
 (2)

where,  $r_1$  is the size of the ion with a larger radius, and  $r_2$  is the size of the ion with a smaller radius. The ionic radii of  $Cr^{3+}$  and  $Zr^{4+}$  are 0.615 Å and 0.84 Å, respectively. The difference value between ionic radii calculated by Eq. 1 was 26.78%, which is between 15% and 30%. Therefore, the solid solution type formed by the introduction of Cr is a finite solid solution with a maxi-

mum value of doping content. The solution equation is the following:

$$2\operatorname{Cr}_2\operatorname{O}_3 \xrightarrow{\operatorname{ZrSiO}_4} 2\operatorname{Cr}_{\operatorname{Zr}}^{\bullet} + 3\operatorname{O}_0 + V_0^{\bullet\bullet}$$
(3)

Additionally, it can be found from the local magnification of the (200) crystal plane of zircon phase (JCPDS No. 06-0266), that the diffraction peaks of Cr-V codoping samples shift in comparison with the sample without Cr-doping. The ion radii of  $^{[VI]}Cr^{3+}$  (0.615Å) and  $^{[VIII]}V^{4+}$  (0.72 Å) are smaller than that of  $^{[VIII]}Zr^{4+}$ (0.84 Å) and the bond length of Zr–O is close to Cr–O [22].  $^{[VIII]}Zr^{4+}$  (0.84 Å) is easily replaced by  $^{[VI]}Cr^{3+}$ (0.615 Å). However, this is inconsistent with the results. These results suggest that the co-doping of V ion with the formation of (Cr,V)-ZrSiO<sub>4</sub> pigment. Recent studies [11,23] have shown that  $V^{4+}$  exists in the interstitial site (16g) in the ZrSiO<sub>4</sub> lattice. Therefore, as the Cr/Si molar ratio increases, the diffraction peaks of samples shift to lower angles and it can be attributed to the mutual promotion of Cr-V solid solutions in the lattice [24]. However, the displacement near the peak corresponding to (200) plane does not shift to a lower angle with the Cr/Si molar ratio 0.4, indicating that the Cr amount reaches the maximum.

Figure 3 exhibits chromaticity values of the samples with different Cr/Si molar ratios, and the inner inserted illustrations are the physical graphs of the samples. The colour of the pigments changes from blue to jewel green and then to dark green, with the increase of Cr/Si molar ratio from 0 to 0.4. The sample without Cr-doping shows the sky blue colour due to the reduction of V<sup>5+</sup> to V<sup>4+</sup> [22] which dissolves in the ZrSiO<sub>4</sub> lattice to form V-ZrSiO<sub>4</sub>. The introduction of Cr-doping promotes the formation of (Cr,V)-ZrSiO<sub>4</sub> solid solution, due to the presence of (V)-ZrSiO<sub>4</sub> in which vanadium plays the both roles of mineralizer and dopant. The extrinsic electron configuration of Cr  $(1s^22s^22p^63s^23p^63d^34s^1)$  is similar to that of V  $(1s^22s^22p^63s^23p^63d^34s^2)$ . After Cr-doping, the whole energy band is shifted, and the Fermi



Figure 3. Chromaticity values of pigments with different Cr/Si molar ratios and physical graphs

energy level enters the conduction band. The band gap narrows with the formation of an electron transition ladder, which is conducive to the visible light absorption [25]. More Cr ions enter into the lattice of  $ZrSiO_4$  with the increase of Cr/Si molar ratio. According to the data shown in Fig. 3, the sample without Cr-doping appears in sky blue colour. The  $L^*$  and  $a^*$  values decrease gradually, and the value of  $b^*$  decreases at first and then increases with the increase of Cr-doping content. This indicates that the increase of Cr/Si molar ratio can increase the greenness values of the pigments. However, Cr<sub>2</sub>O<sub>3</sub> heterophase appears in the sample with the Cr/Si molar ratio of 0.4, and the change of greenness value is not obvious.  $Cr_2O_3$  heterophase gives the pigment an overall black hue. Therefore, the optimized Cr/Si molar ratio is 0.2 in the investigated Cr-doping content range, at which the (Cr, V)-ZrSiO<sub>4</sub> pigments possess optimized performance. This pigment shows a typical jewel green with  $L^* = 56.69$ ,  $a^* = -18.52$ , and  $b^* = -9.28$ .

Figure 4 shows the SEM and TEM images of the sample with Cr/Si molar ratio of 0.2. As it can be seen in Fig. 4, the particle distribution of the pigments is relatively uniform. The surface of the pigment is dense with distinctive edges and crystal faces, and the average particle size is about 2–6  $\mu$ m. Figure 5 shows the particle size distribution of the sample with Cr/Si molar ratio of 0.2. The  $D_{50}$  of the pigment is 3.29  $\mu$ m. In addition, the

particle size distribution of the pigment is narrow, which is consistent with the particle size observed in the SEM image shown in Fig. 4. These results indicate that the optimized (Cr,V)-ZrSiO<sub>4</sub> pigment has appropriate and relatively uniform particle sizes for glazing.

## 3.2. Stability and near-IR reflection performance

Figure 6 shows the photographs of the pigment and glazing sample. The glazing sample is obtained by adding 5 wt.% (mass percentage of transparent glaze) pigment into the transparent glaze, applying it to the blank body and then calcining at 1200 °C for 30 min with the heating rate of 5 °C/min. It can be seen from this figure that the glaze exhibits a smooth and glassy surface. In addition, the hue of glazing sample matches well with the hue of the pigment itself, and they both show a typical jewel green. This suggests that the pigment has excellent chemical and thermal stability.

The glazing sample is subjected to the visible and near-infrared reflection performance test. Figure 7 shows the reflectivity curves of glazing sample with the Cr/Si molar ratio of 0.2 and 0. As it can be seen from Fig. 6, the glaze with (Cr,V)-ZrSiO<sub>4</sub> pigment has high reflection characteristics at 400–2500 nm. The visible light band in the range of 435–469 nm corresponds to indigo, and 469–550 nm corresponds to a typical jewel green. The reflection edge undergoes a red shift as the Cr/Si molar ratio increases, resulting in relatively low  $a^*$ 



Figure 5. Particle size distribution of pigment with Cr/Si molar ratio of 0.2



Figure 4. SEM (a,b) and TEM (c) of pigment with Cr/Si molar ratio of 0.2



Figure 6. Digital photograph of pigment with Cr/Si molar ratio of 0.2 and its glaze sample



Figure 7. Reflectivity curves of glazing samples with Cr/Si molar ratio of 0.2 and 0

values. When the Cr/Si molar ratio is 0.2, it approaches the green light region. The wavelength range of 700– 780 nm corresponds to the red band. Furthermore, the reflection band at >780 nm corresponds to the nearinfrared band. The average reflectivity in the wavelength range of 780–2500 nm reaches 65% when the Cr/Si molar ratio is 0.2, indicating a typical near-infrared reflection. The reflectivity is still increasing with the increase of wavelength, indicating that the (Cr,V)-ZrSiO<sub>4</sub> pigment possesses appreciable near-infrared reflection performance.

## **IV.** Conclusions

Novel (Cr,V)-ZrSiO<sub>4</sub> jewel green pigments were synthesized by *in situ* mineralization at 900 °C. The results show that with the increase of Cr/Si molar ratio from 0 to 0.4, the colour of the pigment changes from blue to jewel green and then to dark green.  $Cr_2O_3$  is used as colourant, and Na<sub>3</sub>VO<sub>4</sub> acts as mineralizer and composite colourant. The appropriate amount of Cr-V codoping can effectively promote the growth and development of ZrSiO<sub>4</sub> crystal. The optimized Cr/Si molar ratio of 0.2 results in a typical jewel green with  $L^* = 56.69$ ,  $a^* = -18.52$  and  $b^* = -9.28$ . The average particle size of pigment was about 2–6 µm, which is suitably applied to ceramic glaze and shows good thermal stability. Furthermore, the average reflectivity in the wavelength range of 780–2500 nm reaches 65%, showing good near-infrared radiation performance. The properties make (Cr,V)-ZrSiO<sub>4</sub> pigments to have a broad application prospects in heat insulation.

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