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Preparation of Cr_2O_3-based pigments with high NIR reflectance via thermal decomposition of CrOOH

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Abstract: In order to reduce greenhouse gas emission and urban heat island mitigation, pure and titanium(Ti)-doped Cr_2O_3 cool pigments were prepared via the thermal decomposition of CrOOH. The result reveals that the pure Cr_2O_3 pigment presents both a high near-infrared reflectance and excellent yellowish-green color. Meanwhile, titanium was doped to improve the NIR reflectance and strengthen the color. The color of the designed pigments was brighter, and most importantly, the NIR reflectance increased from 84.04% to 91.25% with increasing Ti content from 0 to 0.006% (mole fraction). However, excessive doping of Ti^{4+} for Cr^{3+} in Cr_2O_3 (x(Ti)≥0.008%) decreased the NIR reflectance. One possible reason is that the conductivity type of the $Cr_{2-x}Ti_xO_{3+\delta}$ changed from p-type conduction to n-type conduction with increasing Ti content, accompanied by the change of the electrical resistivity and the NIR reflectance. The prepared yellowish-green Cr_2O_3 pigments have a great potential for extensive applications in construction and military.
Key words: CrOOH; cool pigments; NIR reflectance; Ti-doped Cr_2O_3

1 Introduction

The world is facing disruptive global climate change from greenhouse gas emission and increasingly expensive energy supplies. Cool pigments that absorb less near-infrared reflecting (NIR) radiation provide a number of benefits, including reduced energy use and greenhouse gas emission, urban heat island mitigation [1−3]. Therefore, cool pigments have been used in the construction, military and plastics [4]. As one of the green pigments, Cr_2O_3 with a high NIR reflectance has been progressively applied to cool roofing pigments [5,6] and green military camouflage paint and netting [7]. It is required to exhibit green color in the visible spectrum, and also simulate the high reflectivity of chlorophyll in the near infrared portions of the spectrum. Therefore, much interest has attended in preparing Cr_2O_3 with a high NIR reflectance and green color performance.

The industrial production procedures of the high NIR reflectance Cr_2O_3 pigment employ conventional techniques: the thermal decomposition of CrO_3 [8,9] and the reduction of alkali metal chromate with ammonium sulfate [10]. There are serious problems with the traditional production procedures including the environmental pollution resulted from Cr(VI)-containing dusts, and the expensive cost [11−14]. Thus, there is a strong incentive to develop colored, high NIR reflectance Cr_2O_3 pigments through a green production that is less hazardous to environment.

The NIR reflectance of pure Cr_2O_3 was in the range of 50% to 57% [15,16]. After small amounts of metal

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ions, such as Al, Ti, V, Co and Bi, are normally introduced into the Cr_2O_3, the modified Cr_2O_3 produced an excellent NIR reflectance (70%−82%) [17−20]. The doping with rare earths, such as La and Pr, which have been reported to be environmentally benign, resulted in nano-oxides with high reflective properties (85%) [21−24]. However, the chromatic properties of these resulting high NIR reflectance products are single dark-green and unsatisfactory. Moreover, the reason why doping of other metal elements in a host component Cr_2O_3 significantly changes the NIR reflectance has been seldom reported previously.

In this work, we try to do four works: 1) preparing pure Cr_2O_3 through a non-toxic and convenient process which does not produce Cr(VI)-containing dusts; 2) improving the NIR reflectance of pure Cr_2O_3 from 50%−57% to 84.04%; 3) improving the color performance of Cr_2O_3 from single dark-green to bright yellowish-green while maintaining its high NIR reflectance; 4) discussing the mechanism that doping of other metal element in Cr_2O_3 significantly changed the NIR reflectance. The Cr_2O_3 was prepared from the thermal decomposition of CrOOH. This process was expected to prepare a pure Cr_2O_3 with both high NIR reflectance and good color performance. Finally, Ti has been doped into CrOOH to replace the Cr^{3+} ion and further improve the NIR reflectance. The mechanism that doping of Ti element in Cr_2O_3 changed the NIR reflectance was also discussed.

2 Experimental

CrOOH used in this work was manufactured via hydrogen reduction of K_2CrO_4 [25]. It was calcined in an electric muffle furnace at 1150 °C for a soaking time of 1.5 h and then rapidly cooled. The resulting Cr_2O_3 samples were lixiviated with distilled water. The final products were recovered, generally by filtration and drying.

The $Cr_{2-x}Ti_xO_{3+\delta}$ (x ranges from 0 to 0.02) were synthesized by a solid state reaction method, using precursor CrOOH (99.5%) and TiO_2 (99.9%) as starting materials. Stoichiometric proportions of the precursors were transferred into an agate mortar and homogenized by milling. The resultant powders were calcined in a high temperature electric furnace at an optimized temperature of 1150 °C for 1.5 h. Finally, the Cr_2O_3 products were recovered, generally by filtration and drying.

The color performance data were reported using the CIE $L^*a^*b^*$ (1976) colorimetric system. A Datacolor 110 colorimeter, manufactured by Datacolor CO., Ltd., USA, equipped with an illuminant D65 and 10° complementary observer as required, was employed. The value of CIE-L^* denotes the degree of lightness and darkness of the color in relation to the scale extending from white (L^*=100) to black (L^*=0). The value of CIE−a^* denotes the scale extending from the green ($-a^*$) to red ($+a^*$) axes. The value of CIE-b^* denotes the scale extending from the blue ($-b^*$) to yellow ($+b^*$) axes. For each colorimetric parameter of the analyzed sample, three values were measured, and the average value was chosen as the measurement result.

The optical properties of the samples were then analyzed by diffuse reflectance spectroscopy (UV-Vis-NIR), which was performed using a Perkin−Elmer (lambda 750) spectrophotometer in the wavelength range of 380−2500 nm employing barium sulphate as a reference. The NIR reflectance was calculated in accordance with the ASTM standard EN410 [26]. The solar reflectance (R) in the wavelength range from 780 to 2500 nm can be figured out.

$$R=\frac{\int_{780}^{2500} r(\lambda)i(\lambda)\mathrm{d}\lambda}{\int_{780}^{2500} i(\lambda)\mathrm{d}\lambda} \tag{1}$$

where $r(\lambda)$ is the spectral reflectance obtained from the experiment and $i(\lambda)$ is the standard solar spectrum.

Microstructural characterization of the powders was conducted using a JSM−6700F NT scanning electron microscope (SEM), supplied by JEOL. X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer employing Cu K_α radiation (2θ from 5° to 90°, with steps of 0.02°, and a counting time of 2 s per step).

3 Results and discussion

3.1 Pure Cr_2O_3 pigment sample

The Cr_2O_3 which was prepared by calcining a pure CrOOH at 1150 °C for 1.5 h was named as Sample S_1. Thermal decomposition of CrO_3 was a representative industrial method for the production of Cr_2O_3. Commercial Cr_2O_3 pigment produced by this method was chosen as the standard NIR reflection samples. The reflectance spectra of the Sample S_1 and standard Cr_2O_3 are given in Fig. 1(a). Multiplying the normalized spectral irradiance of the sun $i(\lambda)$ by the spectral reflectivity yields the NIR solar reflection spectrum presented in Table 1. As can be seen in Table 1, the standard Cr_2O_3 exhibited an NIR reflectance of 82.51%. Sample S_1 has a NIR reflectance of 84.04%. The result demonstrates that the Cr_2O_3 prepared from the thermal decomposition of CrOOH has an excellent NIR reflectance.

The absorption spectra of the two samples are also determined and compared in the visible region of 380−

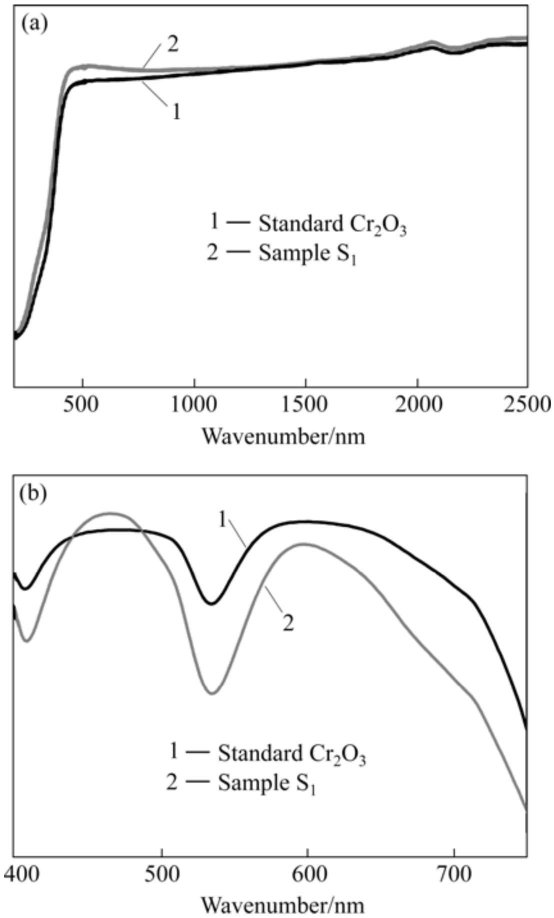

Fig. 1 NIR reflectance (a) and absorption spectra (b) of standard Cr_2O_3 and Sample S_1

780 nm from Fig. 1(b). Both samples show two distinct absorption bands at about 460 nm and 600 nm. According to the Tanabe−Sugano diagram, these bands can be attributed to $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$ (F) spin-allowed transitions, respectively [27]. As can be seen from the absorption spectrum of Cr_2O_3 shown in Fig. 1(b), in Sample S_1, a progressive two-fold splitting of the high absorption band can be seen. Moreover, the absorption edge of sample S_1 is somewhat steep, indicating a very pure and brilliant color. The positions of absorption bands and their intensities and shapes, are important factors in the determination of color. Compared with standard Cr_2O_3, the positions of the absorption edges of Sample S_1 undergo a red-shift, thus the pigment product S_1 exhibits a more yellowish-green color than that of standard Cr_2O_3.

The CIE 1976 color coordinates of the standard Cr_2O_3 and Sample S_1 are shown in Table 1. Compared with the standard Cr_2O_3, Sample S_1 has an increase in the b^* value from 8.88 to 20.38, which shows that the yellowness of the pigment sample is enhanced. At the same time, the increase of the green hue of the Sample S_1 that is evident from the higher values of the color coordinate $-a^*$ (a^* changes from −12.04 to −19.23). The L^* values of the samples are from 38.27 to 47.60. As a result, the Sample S_1 shows an excellent yellowish-green color when compared with the dark-green standard Cr_2O_3. The significant differences in the color performance of the samples can be observed in Fig. 2. Physicochemical properties of Sample S_1 including the stability and capacity to absorb oil and sieve residue were also measured and discussed. The Cr_2O_3 content of Sample S_1 as main chemical composition was more than 99% (mass fraction), and water-soluble matter content was lower than 0.1%, the contents of volatile matter and moisture were lower than 0.15%, the sieve residue content was lower than 0.01%, capacity to absorb oil (g/100g) was 20.98, which were conformed to commercial pigment standard. It was found that Cr_2O_3 which was obtained by

Table 1 Solar reflectance and chromatic coordinates of standard Cr_2O_3 and Sample S_1

Sample	Solar reflectance/%	Color performance			Color
		L^*	$-a^*$	b^*	
Standard Cr_2O_3	82.51	38.27	12.04	8.88	Dark-green
Sample S_1	84.04	47.60	19.23	20.38	Yellowish-green

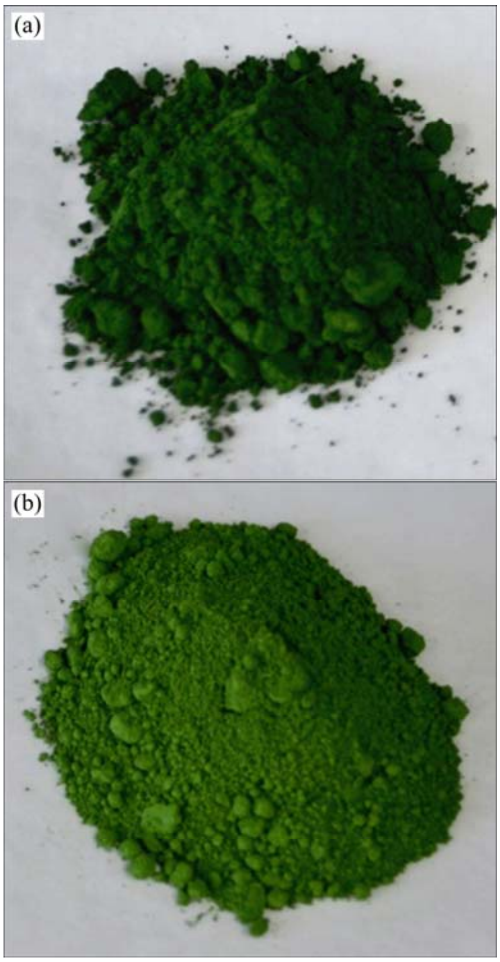

Fig. 2 Photographs of Cr_2O_3 pigments: (a) Standard Cr_2O_3 (dark-green); (b) Sample S_1 (yellowish-green)

calcining the CrOOH has both an excellent yellowish-green color and a commensurate NIR reflectance compared with the standard Cr_2O_3.

The industrial production of the standard Cr_2O_3 pigments employs the thermal decomposition of CrO_3. The different decomposition mechanisms between CrOOH and CrO_3 may result in different morphologies and grain sizes of Cr_2O_3 pigments; as a result, the optical reflections or absorptions of the Sample S_1 and the standard Cr_2O_3 were also different. Earlier investigations showed that the decomposition of CrO_3 into Cr_2O_3 involved the formation of three detectable intermediate phases: $CrO_{2.66}$, $CrO_{2.5}$ and $CrO_{2.25}$ [9], which were previously characterized by XRD and infrared spectroscopy. However, CrOOH showed a sharp exothermic peak centered at 430 °C corresponding to the dehydroxylation of the compound and the crystallisation of Cr_2O_3 [25].

The different decomposition courses of CrO_3 and CrOOH may result in different particle sizes and shapes of Cr_2O_3. The morphology of Sample S_1 is compared with that of standard Cr_2O_3 in Fig. 3. According to Fig. 3(b), the particles of the Sample S_1 had a flat and round shape and well dispersed. These particles are fully crystallized with a uniform size of 300−700 nm. However, when compared with the Sample S_1, the standard Cr_2O_3 turns to be much more irregular. The morphology of standard Cr_2O_3 appears to be cobblestone, with non-uniform particles having diameters ranging from 0.3 to 2.2 μm.

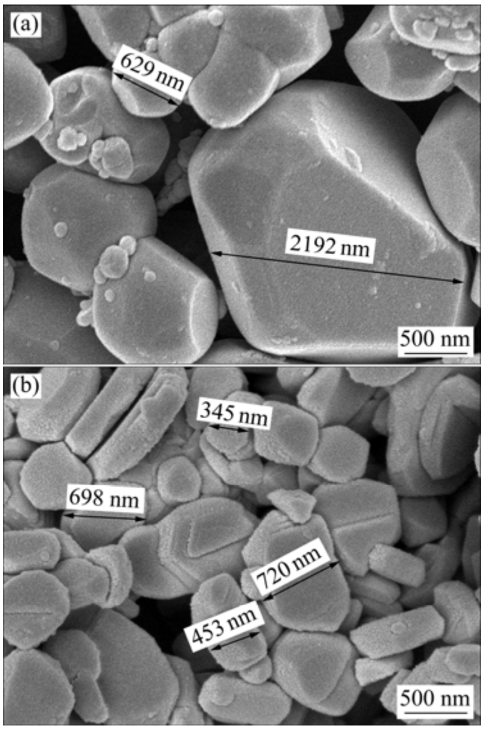

Fig. 3 SEM images of samples: (a) Standard Cr_2O_3; (b) Sample S_1

It is known that when a beam of light falls on a sample, reflection, transmission, and absorption can occur. If the Cr_2O_3 is thick enough, the transmitted light can be neglected. There are many factors that affect the reflectance of pigments, in which the particle size plays a crucial role. When the particle size of Cr_2O_3 decreases from 3 μm to 300 nm, the number of grains in the same volume tends to increase, thus the reflection path of light inside the pigment tends to increase [17]. As a result, the total reflection increases. Thus, the Sample S_1 is more reflective compared with the standard Cr_2O_3. On the other hand, with the particle size of Cr_2O_3 increases, the scattering powder decreases and the color is darker, bluer, and less saturated [28]. From the experimental results, CrO_3 produced a Cr_2O_3 pigment with a large size and dark-green color performance, while Cr_2O_3 obtained by calcining the CrOOH had a yellowish-green color.

CrOOH plays a desirable role in regulating crystal growth and produces a Cr_2O_3 pigment with a uniform size. Cr_2O_3 pigment with a high NIR reflectance and a yellowish-green hue was obtained. The high reflectance exhibited by the designed yellowish-green pigment indicated that this pigment can serve as an excellent cool pigment.

3.2 Ti-doped Cr_2O_3 pigments

In order to further improve the NIR reflectivity of Cr_2O_3 pigments, chrome oxide as a host component containing the element titanium as a guest component has been obtained. It is reported that compared with pure Cr_2O_3, Ti-doped Cr_2O_3 has changed many properties including porous structure, grain size [29], surface area [30], conductivity [31], color performance and NIR reflectivity [24]. Ti-doped Cr_2O_3 has a wide application in sensors to detect trace quantities of reducing gases in air as well by changing its resistance [32].

In this work, CrOOH and TiO_2 were mixed into different compositions and then calcined to obtain $Cr_{2-x}Ti_xO_{3+\delta}$ products. The XRD patterns of the $Cr_{2-x}Ti_xO_{3+\delta}$ (x ranges from 0.003 to 0.02) are shown in Fig. 4. All the patterns show the characteristic reflections of the corundum structure of Cr_2O_3 (JCPDS card No. 38−1479) and no impurity phases are detected. It is probable that Ti forms solid solution with corundum-hematite crystalline structure.

For the $Cr_{2-x}Ti_xO_{3+\delta}$ complex pigment, the electronic transitions of Ti ions result in more absorption and less reflectance in the near infrared region of $Cr_{2-x}Ti_xO_{3+\delta}$. The NIR reflectance spectra of $Cr_{2-x}Ti_xO_{3+\delta}$ prepared are shown in Fig. 5. The titanium free sample exhibits 84.04% NIR reflectance at 780−2500 nm region. Doping of 0.006% Ti^{4+} for Cr^{3+} in Cr_2O_3 increases the NIR reflectance to 91.25%. The NIR reflectance of this sample is superior to that of standard Cr_2O_3. On the other

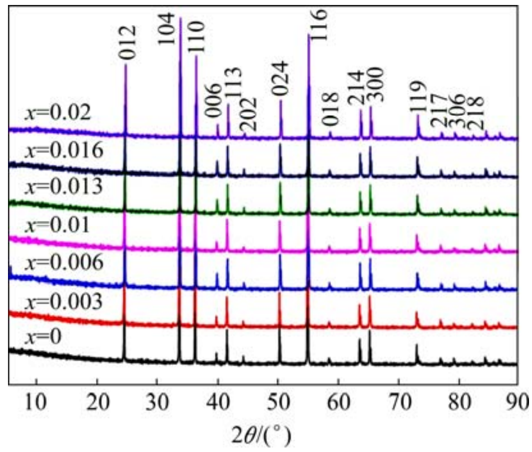

Fig. 4 Powder X-ray diffraction patterns of $Cr_{2-x}Ti_xO_{3+\delta}$ pigments

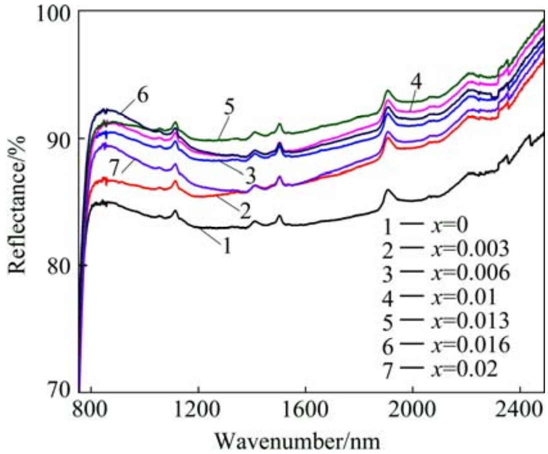

Fig. 5 NIR reflectance spectra of $Cr_{2-x}Ti_xO_{3+\delta}$ pigments

hand, further doping of more Ti^{4+} for Cr^{3+} decreases the NIR reflectance. The high NIR reflectance values highlight the potential for the utility of these samples as cool pigments.

The chromatic properties of the synthesized $Cr_{2-x}Ti_xO_{3+\delta}$ (x ranges from 0 to 0.02) pigments can be assessed from their CIE 1976 color coordinate values depicted in Table 2. The standard Cr_2O_3 pigment was produced from the thermal decomposition of CrO_3, while the Cr_2O_3 of Sample S_1 was also prepared by calcining a pure CrOOH at 1150 °C for 1.5 h. The systematic doping of Ti^{4+} for Cr^{3+} in Cr_2O_3 (n(Ti):n(Cr) from 0 to 1.01%) results in an increase in the L* value regularly from 47.60 to 52.48, which indicates that the brilliant color of the pigment sample is enhanced. On the other hand, the increase of titanium does not seem to affect the green and yellow hue of the pigments. After being doped with titanium, all samples show a bright yellowish-green color.

$Cr_{2-x}Ti_xO_{3+\delta}$ pigments are found to have a more bright yellowish-green color performance and a high NIR reflectance (91.25%). Through Fresnel formula [33], the NIR reflectance has a relationship between refractive index and extinction index, which are determined by the conductivity and the dielectric constant.

The results of some researchers strongly suggest that the introduction of Ti^{4+} to Cr_2O_3 alters its defect structure and electrical conductivity [34]. Cr_2O_3 is usually reported as an insulator with the possibility of low native p-type conductivity [35]. In particular, Ti^{4+}-doped Cr_2O_3 are famous systems in which doping can influence the electronic property. The mixed valence formation of Cr_2O_3 by Ti^{4+} ion doping has been described as follows [36,37]:

$$3TiO_2 \xrightarrow{Cr_2O_3} 3Ti^{\cdot}_{Cr} + V'''_{cr} + 6O_0 \quad (2)$$

$$2TiO_2 \xrightarrow{Cr_2O_3} 2Ti^{\cdot}_{Cr} + O''_{i} + 3O_0 \quad (3)$$

Equation (2) represents compensation of Ti^{4+} by Cr vacancies, and Eq. (3) represents compensation by electrons and can be regarded as dissolution as Ti^{3+} depending on the degree of ionization of the neutral defect. The variation in measured density of the solid solution indicates that Eq. (2) is the main reaction [37]. NAGAI and OHVAYASHI [38], through measurements

Table 2 Solar reflectance and color coordinates of the $Cr_{2-x}Ti_xO_{3+\delta}$ (x ranges from 0 to 0.02)

Sample	Composition	Solar reflectance/%	Color performance			Color
			L*	a*	b*	
Standard Cr_2O_3	Cr_2O_3	82.51	38.27	12.04	8.88	Dark-green
S_1	Cr_2O_3	84.04	47.60	−19.23	20.38	Yellowish-green
S_2	$Cr_{1.997}Ti_{0.003}O_{3+\delta}$	86.45	50.23	−19.83	19.85	Bright yellowish-green
S_3	$Cr_{1.994}Ti_{0.006}O_{3+\delta}$	89.64	50.95	−19.98	20.34	Bright yellowish-green
S_4	$Cr_{1.990}Ti_{0.01}O_{3+\delta}$	90.11	51.61	−19.80	20.04	Bright yellowish-green
S_5	$Cr_{1.987}Ti_{0.013}O_{3+\delta}$	91.25	52.48	−19.79	19.81	bright yellowish-green
S_6	$Cr_{1.984}Ti_{0.016}O_{3+\delta}$	91.05	50.87	−19.31	19.90	Bright yellowish-green
S_7	$Cr_{1.980}Ti_{0.02}O_{3+\delta}$	87.70	49.56	−18.33	18.58	Bright yellowish-green

of electrical conductivity and thermoelectric power of $Cr_{2-x}Ti_xO_{3+\delta}$, reported that undoped Cr_2O_3 had a p-type conductivity, and a change in the conduction behavior of $Cr_{2-x}Ti_xO_{3+\delta}$ from p-type conduction to n-type conduction with increasing the TiO_2 content to more than 1.85% [31,38,39].

Thus, it can be deduced that in this work after doping of Ti^{4+} for Cr^{3+} in Cr_2O_3, the conductivity decreases with the increase of the Ti content from Sample S_1 to sample S_5, accompanied by the change of the NIR reflectance. When doping of 0.006% Ti^{4+} for Cr^{3+} in Cr_2O_3, the conductivity type of $Cr_{1.987}Ti_{0.013}O_{3+\delta}$ (Sample S_5) changed from p-type conduction to n-type conduction. However, excessive doping of Ti^{4+} for Cr^{3+} in Cr_2O_3, the conductivity type of $Cr_{2-x}Ti_xO_{3+\delta}$ is n-type conduction, and the conductivity increases with the increase of the Ti content from Sample S_5 to Sample S_7. At last, the conductivity goes through a minimum and then increases, accompanied by the change of the dielectric constant and the NIR reflectance. So, the NIR reflectance is influenced by the proportion of Ti doping into Cr_2O_3, and the $Cr_{1.987}Ti_{0.013}O_{3+\delta}$ has the highest reflectance (91.25%).

4 Conclusions

1) Cr_2O_3 pigment with a comparable high NIR reflectance and a bright yellowish-green hue was obtained via the simple calcine of CrOOH. The results demonstrated that the produced Cr_2O_3 has a higher NIR reflectance of 84% and good yellowish-green color compared with the dark-green standard Cr_2O_3.

2) Titanium (Ti) was doped to improve the NIR reflectance and a series of $Cr_{2-x}Ti_xO_{3+\delta}$ (x ranges from 0 to 0.02) having a corundum structure displaying color of bright yellowish-green were synthesized by the solid state route. The conductivity type of $Cr_{2-x}Ti_xO_{3+\delta}$ changed from p-type conduction to n-type conduction with Ti doping, and the NIR reflectance increased to the maximum value, and then decreased. As a result, the $Cr_{1.987}Ti_{0.013}O_{3+\delta}$ which displaying a bright yellowish-green color has the highest reflectance of 91.25%.

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热分解 CrOOH 制备具有高近红外反射率的 Cr_2O_3 颜料

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摘 要：为了减少温室气体的排放，缓解城市热岛效应，通过热分解 CrOOH 制备纯 Cr_2O_3 冷色颜料和掺 Ti 的 Cr_2O_3 冷色颜料。结果表明，所制备的纯 Cr_2O_3 颜料同时具有较高的近红外反射性能和优良的黄绿色调。同时，在 Cr_2O_3 中掺杂 Ti^{4+}离子可进一步提高其红外反射率和颜色性能。所制备的 Ti 掺杂 Cr_2O_3 颜料的颜色非常明亮光鲜。随着 Ti 掺杂量由 0 提高至 0.006%(摩尔分数)，样品的近红外反射率由 84.04%提高至 91.25%。然而，Ti^{4+}掺杂量过高(x(Ti)≥0.008%)会使近红外反射率降低，这可能是由于随着 Ti^{4+}含量的升高，$Cr_{2-x}Ti_xO_{3+\delta}$ 的导电性能由 p 型导电转变为 n 型导电，同时伴随电阻率和近红外反射性能的变化。制备的明亮黄绿色调的 Cr_2O_3 颜料在建筑材料和军事方面具有非常广泛的应用前景。

关键词：CrOOH；冷色颜料；红外反射率；Ti 掺杂 Cr_2O_3

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