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Preparation and characterization of Cr_2O_3–TiO_2–Al_2O_3–V_2O_5 green pigment

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Abstract

Green pigments with high near infrared reflectance based on a Cr_2O_3–TiO_2–Al_2O_3–V_2O_5 composition have been synthesized. Cr_2O_3 was used as the host component and mixtures of TiO_2, Al_2O_3 and V_2O_5 were used as the guest components. TiO_2, Al_2O_3, and V_2O_5 were mixed into 39 different compositions. The spectral reflectance and the distribution of pigment powder were determined using a spectrophotometer and a scanning electron microscope, respectively. It was found that a pigment powder sample S9 with a Cr_2O_3–TiO_2–Al_2O_3–V_2O_5 composition of 80, 4, 14 and 2 wt%, respectively, gives a maximum near infrared solar reflectance of 82.8% compared with 49.0% for pure Cr_2O_3. The dispersion of pigment powders in a ceramic glaze was also studied. The results show that the pigment powder sample S9 is suitable for use as a coating material for ceramic-based roofs.

Keywords: Green pigment; Pigment dispersion; Ceramic glaze; Near-infrared reflectance

1. Introduction

Urban areas around the world are experiencing rapid population growth resulting in rapidly increasing energy consumption, particularly by the air conditioners which are widely used in big buildings. Air-conditioning energy saving can be achieved by reducing the temperature of the building envelope, which in turn reduces the heat penetrating into the building. Exterior surface temperatures may be reduced by protecting the building envelope from the heat of solar radiation. Several techniques have been proposed for protection from solar radiation. Among them the use of cool materials has gained much interest during the past few years. Cool materials referred to pigments that have high near infrared (NIR) solar reflectance or low NIR solar absorptance [1] which have been widely used for coatings on roofs and walls [1–3].

There are currently a number of cool materials commercially available for tile roof coating [4–6]. Inorganic pigments are widely used as cool materials for residential roofs. TiO_2 rutile, a white pigment with a high NIR solar reflectance of about 87.0% [4], is the best pigment used for roofing materials. However, the owners of homes with pitched roofs visible from ground level often prefer non-white roofing products for aesthetic reasons [1,3,7].

Chromium oxide (Cr_2O_3) green pigments have already been used in camouflage coatings used by the army to prevent detection of objects. Due to a medium high NIR solar reflectance in the range of 50–57% [4], Cr_2O_3 green pigments have also been used as coating materials for many types of roof to reduce the roof temperature, while simultaneously improving the roof's appearance. Cr_2O_3 green pigments have been developed by various processes by many researchers [8–11]. On account of its somewhat dull and dark green color, various attempts have been made to obtain a brighter green. Based on Cr_2O_3, a wide range of different complex color pigment systems with high NIR reflectance have been developed [4,12–19]. Complex inorganic black pigments are among the most extensively studied pigments to be used for glazes and ceramic bodies [13–15]. On the other hand, very few studies report complex green pigments [13,16,17]. Recently pigments based on rare earth compounds

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have been extensively studied [20–24]. However, the cost of the rare earth compounds used for the synthesis of pigments is rather high and not so economically viable. In addition, most of the owners of homes with pitched roofs in Thailand prefer green roof products. In the present study, new green pigments based on a Cr_2O_3–TiO_2–Al_2O_3–V_2O_5 composition have been synthesized and the ability of these pigments used with ceramic glazes to confer high solar reflectance has also been studied.

2. Experimental

2.1. Pigment preparation

Since the purpose of this study is to synthesize new green pigments of high near infrared reflectance for industrial applications, all materials used are of commercial grade. Cr_2O_3 (Guangzhou Chemicals), a green pigment oxide, was used as a host component and mixtures of TiO_2 (Du Pont Titanium Technologies), Al_2O_3 (Sumitomo Chemicals) and V_2O_5 (Strategic Metals) were used as guest components. TiO_2, Al_2O_3 and V_2O_5 were mixed into 39 different compositions (denoted as samples S1–S39) as shown in Table 1. For each sample preparation, 80 wt% of Cr_2O_3 was mixed with 20 wt% of guest component. The mixed guest components shown in Table 1 can be classified into 10 groups. Typically, for group 1 the amount of TiO_2 was fixed at 2 wt% whereas the amounts of Al_2O_3 was varied from 16 to 2 wt% and V_2O_5 was varied from 2 to 16 wt%, respectively to make up 20 wt% of guest component. All mixed samples were calcined at 1150 °C for 30 min by applying heat at a rate of 4 °C/min and cooled down naturally to ambient temperature. The samples were milled in an agate ball mill for 7 min at a speed of 250 rev/min and then baked at 110 °C for 30 min to release water. Finally, the pigments were sieved to obtain the particle sizes of 0.5–2.0 μm.

2.2. Spectral reflectance measurements of pigment powders

The pigment powders were compressed in a mold to obtain the sample in a form of thin disk with a diameter of 2.7 cm and a thickness of 4 mm. The spectral reflectance of the samples was measured using a UV–Vis–NIR spectrophotometer (Shimadzu, 3100) in the wavelength range from 300 to 2100 nm. The spectral reflectance data were used to calculate the solar reflectance of each sample. The NIR solar reflectance in the wavelength range from 780 to 2100 nm was calculated in accordance with the ASTM standard number E891-87. According to this standard number the solar spectral irradiances at wavelengths between 0.305 and 4.045 μm are given. Then, the NIR solar reflectance (R) or the fraction of solar radiation incident at wavelengths between 780 and 2100 nm that is reflected by a surface is the irradiance-weighted average of its spectral reflectance, $r(\lambda)$, can be determined that is,

$$R = \frac{\int_{780}^{2100} r(\lambda) i(\lambda) \mathrm{d}\lambda}{\int_{780}^{2100} i(\lambda) \mathrm{d}\lambda} \quad (1)$$

Table 1
The NIR solar reflectance in the wavelength range from 780 to 2100 nm of pigment powder samples S1–S39. For comparison, a pure Cr_2O_3 was also tested.

Group	Sample	Composition (wt%)				Solar reflectance (%)	Color
		Cr_2O_3	TiO_2	Al_2O_3	V_2O_5		
1	S1	80	2	16	2	75.2	Green
	S2	80	2	14	4	75.6	Green
	S3	80	2	12	6	50.0	Green
	S4	80	2	10	8	50.5	Yellowish green
	S5	80	2	8	10	46.9	Yellowish green
	S6	80	2	6	12	44.8	Yellowish green
	S7	80	2	4	14	48.6	Brownish green
	S8	80	2	2	16	52.2	Brownish green
2	S9	80	4	14	2	82.8	Green
	S10	80	4	12	4	71.7	Green
	S11	80	4	10	6	50.0	Green
	S12	80	4	8	8	44.9	Yellowish green
	S13	80	4	6	10	43.1	Brownish green
	S14	80	4	4	12	46.4	Brownish green
	S15	80	4	2	14	48.3	Brownish green
3	S16	80	6	12	2	78.5	Green
	S17	80	6	10	4	70.0	Green
	S18	80	6	8	6	52.4	Green
	S19	80	6	6	8	44.6	Yellowish green
	S20	80	6	4	10	43.7	Brownish green
	S21	80	6	2	12	45.5	Brownish green
4	S22	80	8	10	2	71.1	Green
	S23	80	8	8	4	71.8	Green
	S24	80	8	6	6	63.7	Green
	S25	80	8	4	8	46.1	Yellowish green
	S26	80	8	2	10	43.0	Brownish green
5	S27	80	10	8	2	67.5	Green
	S28	80	10	6	4	69.0	Green
	S29	80	10	4	6	63.2	Green
	S30	80	10	2	8	68.5	Yellowish green
6	S31	80	12	6	2	62.9	Green
	S32	80	12	4	4	60.1	Green
	S33	80	12	2	6	67.6	Green
7	S34	80	14	4	2	60.0	Green
	S35	80	14	2	4	68.4	Green
8	S36	80	16	2	2	49.1	Green
9	S37	80	18	2	–	60.3	Light green
	S38	80	18	–	2	58.6	Light green
10	S39	80	20	–	–	50.2	Light green
	Cr_2O_3	100	–	–	–	49.9	Green

where $r(\lambda)$ is the spectral reflectance (W m^{-2}) obtained from the experiment and $i(\lambda)$ is the solar spectral irradiance (W m^{-2} μm^{-1}) obtained from ASTM standard number E891-87.

The NIR solar reflectance for all samples and pure Cr_2O_3 as determined by Eq. (1) are shown in Table 1. It is seen that, the pigment powder samples S9 and S26 yield a maximum and a minimum NIR solar reflectance of 82.8% and 43%, respectively. Therefore, further characterizations were carried out only on these two pigment powders and pure Cr_2O_3 powder for comparison.

2.3. Crystal structure characterization

The crystal structure of the pigment powder samples S9, S26 and pure Cr_2O_3 was characterized by a X-ray diffractometer (Bruker, D8 Advance) with Cu Kα radiation, 40 kV, 20 mA at 0.02° per step with a step time of 2 s and a scan time of 1.23 h. The XRD patterns were recorded in the 2θ range of 20–70°.

2.4. Color measurement

The pigment powder samples S9, S26 and pure Cr_2O_3 in a form of thin disk obtained in Section 2.2 were also used for color measurement. The color measurement in CIE L^* a^* b^* color scale was performed using a UV–Vis–NIR spectrophotometer (Shimadzu,,3100). The measuring parameters were carried out in reflectance mode with a slit width of 2.0 μm. This measurement was baseline with $BaSO_4$ and the color was measured in the wavelength range of 380–780 nm.

2.5. Distribution of pigment powder

The distribution of pigment powder samples S9, S26 and pure Cr_2O_3 was investigated by a scanning electron microscope (Philip, XL30). In the experiment, the pigment powder samples S9, S26 and pure Cr_2O_3 were prepared on carbon tapes.

2.6. Dispersion of pigment powder in ceramic glaze

In order to examine the dispersion of the pigment powder samples S9, S26 and pure Cr_2O_3 in the ceramic glaze, 6 g of each pigment powder sample was mixed with 100 g of a commercial ceramic glaze (Dayang Glaze). The mixtures were ground in water by a ball mill at a speed of 100 rev/min for 10 min to obtain very homogenous slurries with a specific gravity of about 1.40. It was found that at this specific gravity value, the slurry is composed of 44.4 wt% solid and 55.6 wt% water.

Each prepared sample was sprayed on a ceramic tile of dimension 5 cm × 5 cm by a spray gun of diameter 0.1 mm and with a spraying time of 20 s. The coated ceramic tiles were heated at a rate of 4 °C/min until a maximum temperature of 1100 °C was reached where it was held for 30 min. Then, the coated ceramic tiles were cooled down in air to room temperature. The thickness of coated ceramic tiles was measured and it was found to be about 200 μm.

The coated ceramic tiles obtained above were divided into two parts. One part was used for reflectance measurement by UV–Vis–NIR spectrophotometer and for crystal structure by XRD technique. The other one was sputtered with gold for surface morphology study by SEM.

3. Results and discussion

3.1. NIR reflectance of pigment powder

The reflectance spectra of some pigment powder samples and of pure Cr_2O_3 in the wavelength range from 300 to 2100 nm are shown in Fig. 1. Their corresponding NIR solar reflectances

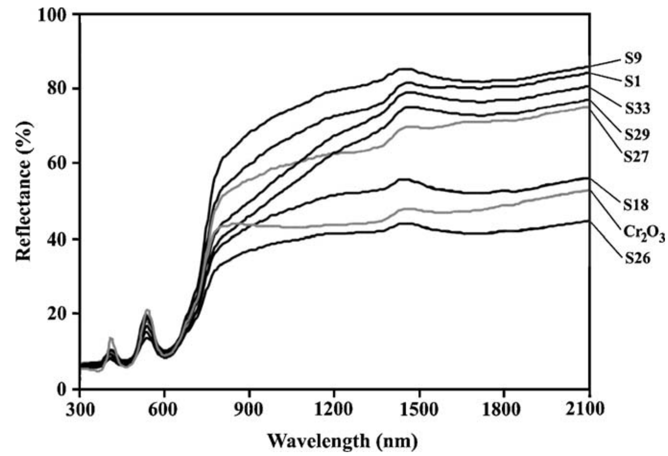

Fig. 1. Showing the reflectance spectra of some pigment powder samples.

in the wavelength range of 780–2100 nm for all pigment powder samples and of pure Cr_2O_3 are shown in Table 1.

As can be seen in Table 1, the NIR solar reflectance having a maximum reflectance of 82.8% and a minimum reflectance of 43.0% were obtained for the pigment powder samples S9 and S26, respectively. As the results, it can be concluded that the significantly increasing of NIR solar reflectance for pigment powder sample S9 prepared in this work is due to the composition of guest components. A conventional pure Cr_2O_3, dull green color, from the measurement result yielded a NIR solar reflectance of 49.9%. When TiO_2 was the solely guest component mixed with 80% of Cr_2O_3 indicated as sample S39, the NIR solar reflectance was 50.2%, nearly the same as for the conventional Cr_2O_3.

3.2. Crystal structure of pigment powder

Fig. 2 shows the XRD patterns of pigment powder samples S9, S26 and pure Cr_2O_3. For the sample S9, the peaks of Cr_2O_3 (80 wt%) and Al_2O_3 (14 wt%) are clearly observed. However,

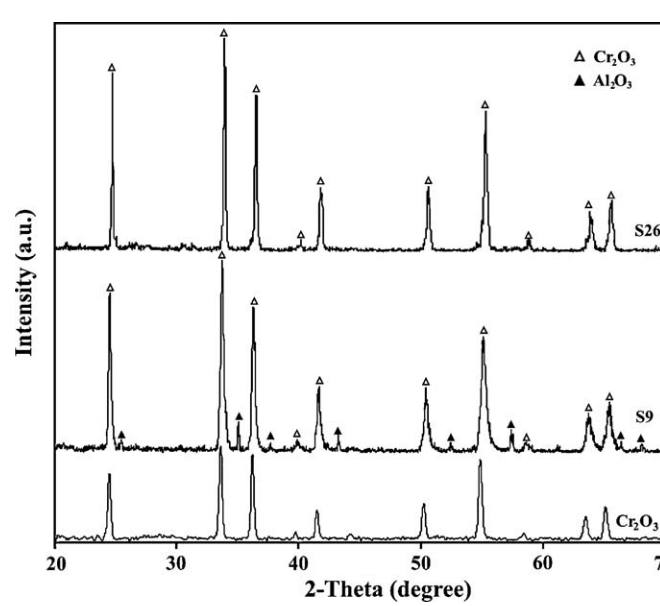

Fig. 2. XRD patterns of pigment powder samples S9, S26 and pure Cr_2O_3.

Table 2
Showing the color index of pigment powder samples S9, S26 and pure Cr_2O_3.

Sample	L^*	a^*	b^*
Cr_2O_3	42.15	−14.44	17.43
S9	58.41	−16.41	18.28
S26	44.07	−7.08	10.94

no peaks of TiO_2 and V_2O_5 appeared due to the lesser amounts of TiO_2 (4 wt%) and V_2O_5 (2 wt%) exist in the composition. The sample S26 shows the peaks of Cr_2O_3 only, no peaks of TiO_2 (8 wt%), Al_2O_3 (2 wt%), and V_2O_5 (10 wt%) were observed. The XRD patterns of samples S9 and S26 revealed that Cr_2O_3 and guest compounds were not melt to form solid solution but they are in the form of compound powders.

3.3. Results on color measurement

Table 2 shows the CIE L^* a^* b^* color index of pigment powder samples S9, S26 and pure Cr_2O_3. The values obtained for all samples fall within green of the color index scale. However, the sample S9 yields highest brightness value (L^*) which result in the brighter green of sample S9 than those of S26 and pure Cr_2O_3.

3.4. Results on the distribution of pigment powder

SEM micrographs of pigment powder samples S9, S26 and pure Cr_2O_3 obtained at magnifications of 2000× and 20,000× are shown in Fig. 3(a) and (b), respectively. Fig. 3(a) shows more uniform distribution of pigment powder sample S9 than that of S26. Furthermore, the distribution of pigment powders is clearly observed in Fig. 3(b). It can be pointed out that the distribution of pigment powder sample S9 is also more uniform distribution than that of pure Cr_2O_3. The presence of the agglomerates in pigment powder sample S26 and pure Cr_2O_3, results in poorer reflectance value of those samples as confirmed in Table 1.

3.5. Results on the dispersion of pigment powder in ceramic glaze

The ceramic tiles coated with the mixture of ceramic glaze and pigment powder samples S9, S26 and pure Cr_2O_3 were investigated by SEM. Fig. 4 shows SEM micrographs of the coated ceramic tiles at 2500× magnification. It can be observed that the pigment powder sample S9 in a ceramic glaze dispersed well over ceramic tiles and yield the best homogeneity of the coated surface.

The spectral reflectance of the coated ceramic tiles was also measured and the results are shown in Fig. 5. Then, the NIR solar reflectance in the wavelength range 780–2100 nm were determined. The NIR solar reflectance of the coated ceramic tiles for ceramic glaze mixed with pigment powder samples S9, S26 and pure Cr_2O_3 were found to be 76.3%, 39.7% and 44.1%, respectively. It is seen that the NIR solar reflectance for pigment powder mixed with a ceramic glaze were slightly lower than those of the corresponding pigment powders. However, a NIR solar reflectance of 76.3% for

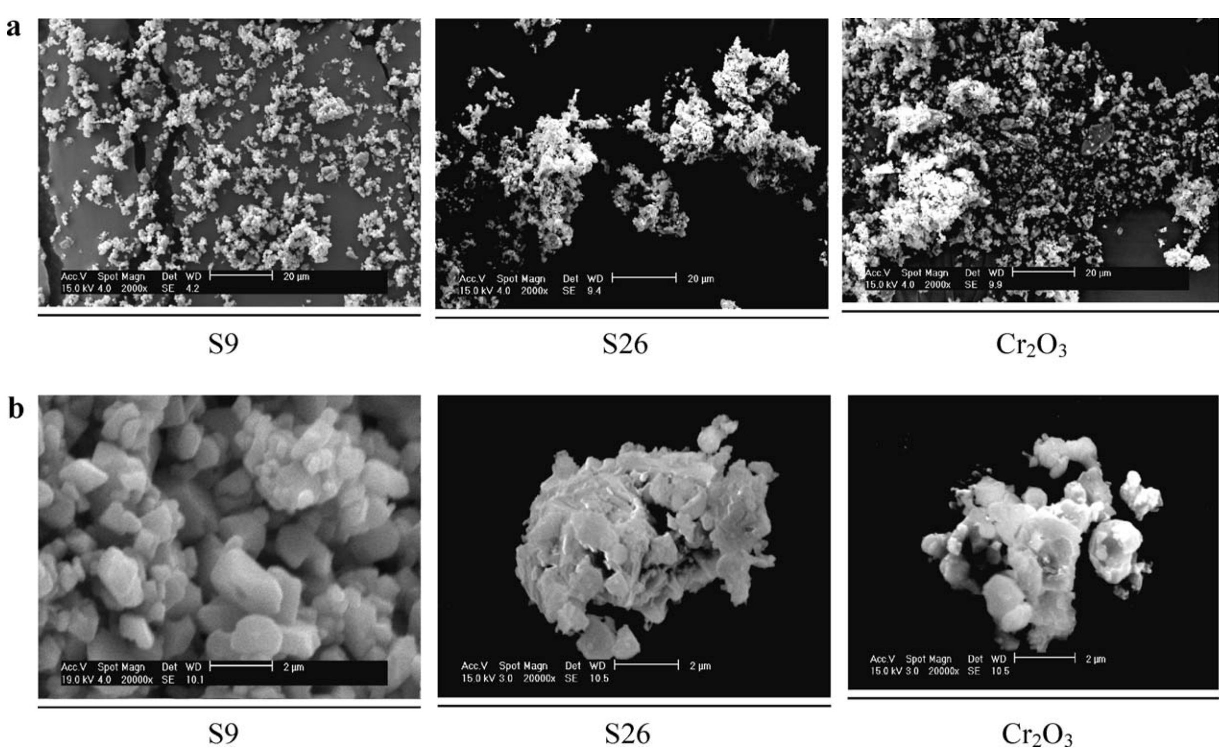

Fig. 3. SEM micrographs of pigment powder samples: (a) at 2000× magnification of S9, S26 and pure Cr_2O_3 and (b) at 20,000× magnification of S9, S26 and pure Cr_2O_3.

a

b

c

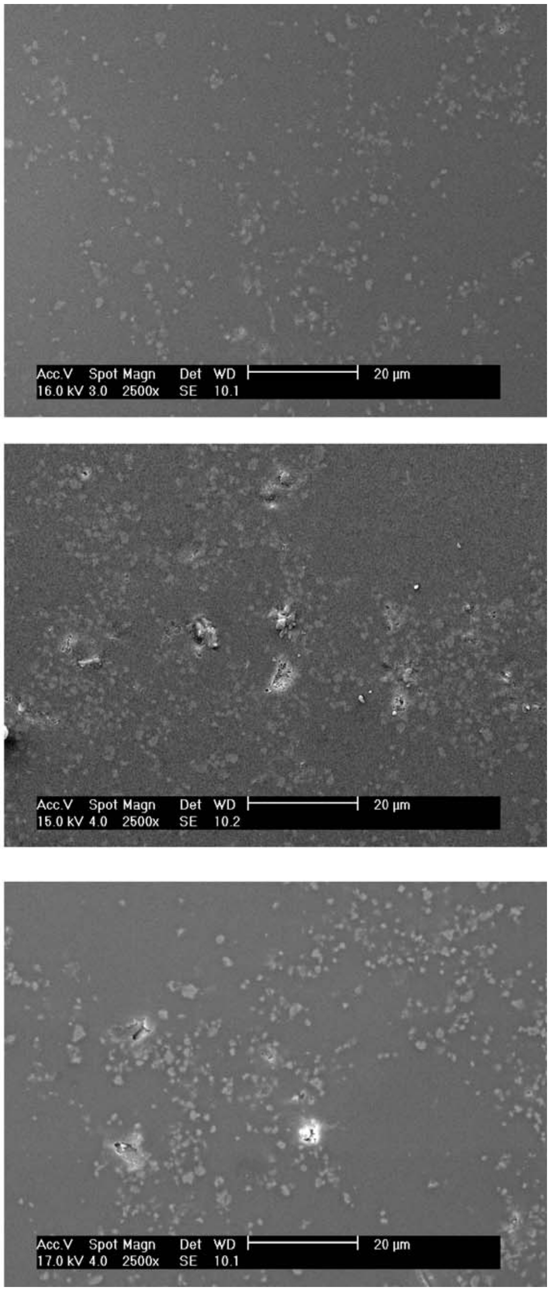

Fig. 4. SEM micrographs at 2500× magnification of ceramic glaze surfaces: (a) glaze containing pigment S9, (b) glaze containing pigment S26, and (c) glaze containing pure pigment Cr_2O_3.

pigment powder sample S9 mixed with the ceramic glaze is significantly high compared with that of pure Cr_2O_3.

The XRD patterns of pure ceramic glaze and the mixture of ceramic glaze and pigment powder samples S9, S26 and pure Cr_2O_3 are shown in Fig. 6. No XRD peaks appeared for pure ceramic glaze indicating that it is amorphous. Furthermore, for the mixture of ceramic glaze and pigment powder samples S9, S26 and pure Cr_2O_3 only the peaks of Cr_2O_3 is observed due to the less amounts of TiO_2, Al_2O_3 and V_2O_5. It can be concluded that Cr_2O_3 did not dissolved into the ceramic glaze.

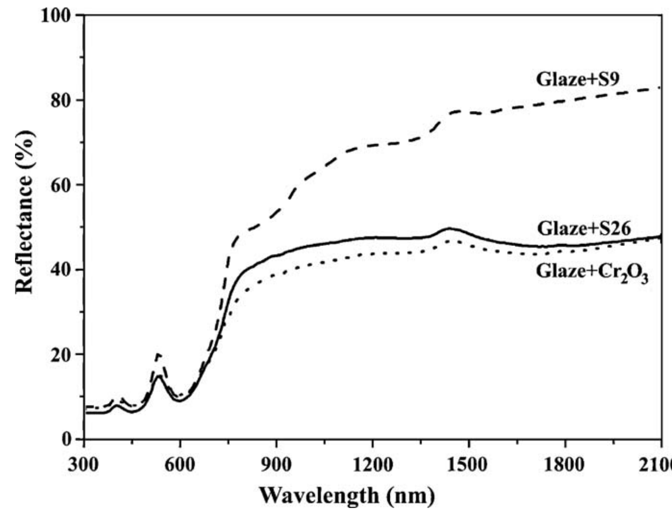

Fig. 5. Spectral reflectance of coated ceramic tiles.

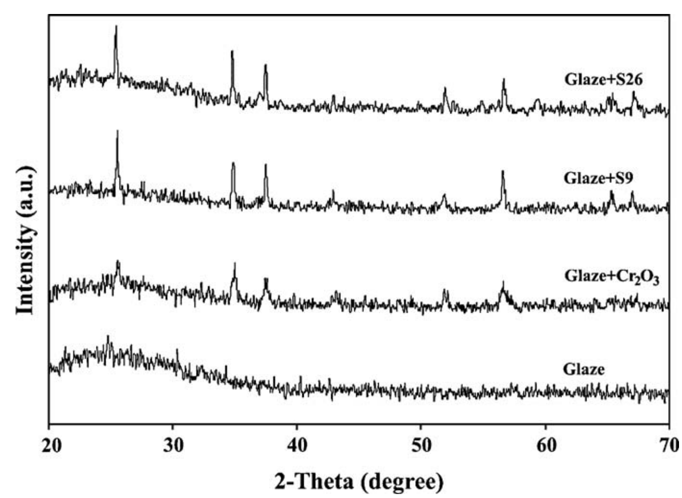

Fig. 6. XRD patterns of pigment powder samples S9, S26 and pure Cr_2O_3 in glaze.

4. Conclusions

Green pigments having a high NIR solar reflectance for roofing materials have been developed. Pigment powders were prepared from Cr_2O_3 and mixtures of TiO_2, Al_2O_3, and V_2O_5. The composition of host component, Cr_2O_3, was fixed at 80 wt% and mixed into 39 different compositions of 20 wt% of TiO_2, Al_2O_3, and V_2O_5. All the prepared samples were calcined at 1150 °C for 30 min. The reflectance spectra show that the sample S9 with a Cr_2O_3–TiO_2–Al_2O_3–V_2O_5 composition of 80, 4, 14 and 2 wt%, respectively has a maximum NIR solar reflectance of 82.8%. The significantly increasing of NIR solar reflectance for pigment powder sample S9 prepared in this work is due to the composition of guest components and a high uniform distribution of the pigment powders. Furthermore, it was found that the dispersion of pigment powder sample S9 in a ceramic glaze is more homogeneous than that of pure Cr_2O_3. The NIR solar reflectance of a coated ceramic substrate for a mixed ceramic glaze with S9 is 76.3% comparing to 49.0% for

Cr_2O_3. It can be concluded that the pigment sample S9 is a suitable coating material on ceramic-based roofs to reflect the heat from penetrating into the building.

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