Effect of Co and Pr doping on the properties of solar-reflective ZnFe$_2$O$_4$ dark pigment

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Abstract. High NIR-reflective Co-doped ZnFe$_2$O$_4$ black pigments were synthesized by a simple solid-state reaction of ZnO and Fe$_2$O$_3$ in the presence of 3 to 30 wt.% Co$_3$O$_4$ at 1000 and 1100 °C. A series of black pigments with low $L^*$ values in a range of 25.5-26.5 and NIR reflectance of 39.5-48.7% were obtained at 1000 °C while the pigments with comparable $L^*$ values and slightly lower NIR reflectance were obtained at 1100 °C. A change of the pigment property could be attributed to substitution of Co$^{2+}$ for Zn$^{2+}$ as revealed by XRD analysis as well as reflectance spectra. Calcination of ZnO and Fe$_2$O$_3$ in the presence of 3 to 30 wt.% Pr$_6$O$_{11}$ at 1100 °C resulted in dark brown composite pigments consisting of ZnFe$_2$O$_4$, PrFe$_2$O$_3$ and unreacted Fe$_2$O$_3$ with $L^*$ value around 40 ±1 and NIR reflectance in a range of 48-50%.

Keywords: Solar-reflective pigment; Near-infrared reflectance; Complex inorganic color pigment; Solid-state reaction

1. Introduction

Heat accumulated in surroundings of densely urban areas caused by the heat released by cars, air-conditioning systems as well as buildings and pavements has a significant impact on the ‘urban heat island effect’. The increased urban temperature intensifies the use of a large amount of overall cooling load, the demand for peak electricity and the amount of greenhouse gases in the atmosphere. Solar energy is absorbed by construction buildings and cement surfaces, leading to an increase of those surface’s temperature as portion of the absorbed energy is radiated back to the atmosphere. It has been reported that energy utilization in the buildings is a substantial portion of total energy consumption [1-3]. In principle, this problem can be reduced by increasing the green areas and selecting a proper design of the buildings for better air circulation. However, these approaches may not be practical for growing urbanized areas. A more practical alternative concerns with the use of suitable building envelopes such as insulating walls and roofs which can retard the heat that is absorbed and built-up inside the buildings. Nevertheless, the heat absorbed by insulated materials will be gradually released into the building.

A new approach of using solar-reflective coating for roof and pavement has been recently introduced to reflect solar radiation, particularly in the near-infrared (NIR) region, thus reducing the heat to be absorbed and transferred into the buildings [4-7]. The coating is formulated by adding an NIR-reflective pigment of desired color in addition to typical colorants. The solar-reflective pigments of various colors, such as green [8], yellow-brown [9-13], and reddish brown and reddish orange [14], have been synthesized. The desired colors were synthesized by doping various dopants into the parent
composite oxide. For example, doping the $\text{Si}^{4+}$ into the $\text{Y}_3\text{MoO}_8$ resulted in bright yellow color while doping with the $\text{Pr}^{4+}$ resulted in red-brown color [13]. Similarly, yellow color was obtained by doping the $\text{Sm}_3\text{Ce}_2\text{O}_7$ with the $\text{Mo}^{6+}$ while brown color was obtained by doping with the $\text{Pr}^{4+}$ [11].

It is well known that white pigments such as titanium dioxide ($\text{TiO}_2$) has high NIR reflectance of about 90% while black pigments such as carbon black has low NIR reflectance of almost 0. However, the use of $\text{TiO}_2$ white pigment is limited to wall coating. Colored NIR-reflective pigments are preferred for roof and pavement. Moreover, NIR-reflective dark pigments are required for roof coating and glaze in which dark color hue is most popular. Therefore, it becomes a very interesting topic based on academic viewpoint, and there is a challenge of making dark pigment with high NIR reflectance. To our knowledge, there are only few literatures reporting the synthesis of dark-brown/ black NIR-reflective pigments [15-17]. Dark brown Zn, Al-doped CoCr$_2$O$_4$ pigment has been synthesized by a sol-gel method [15]. The resultant Co$_{1-x}$Zn$_x$Cr$_2$O$_4$ pigment had color parameter $L^*$ in a range of approximately 54-60 ($L^* = 0$ for absolute black, $L^* = 100$ for absolute white) and NIR reflectance in a range of 44.5-52.1% depending on the amount of Zn dopant. Similarly, the CoCr$_2$Al$_2$O$_4$ pigment had $L^*$ value in a range of 48.6-51.6 and NIR reflectance in a range of 43.5-43.9% depending on the amount of Al dopant. A sol-gel method was also employed to synthesize dark brown Mg-doped ZnFe$_2$O$_4$ pigment [16]. Doping of Mg in zinc ferrite results in a change of color hue from brick red to dark brown with color parameter $L^*$ of approximately 48-49 and NIR reflectance in a range of 51-58% depending on the amount of Mg dopant. A series of brownish-black, greenish-black, black blue and black NIR-reflective pigments with $L^*$ of approximately 23-45 and reflectance of 18.0-51.4% in the Vis-NIR regions (300-2500 nm) were obtained from (CoO)$_x$(MgO)$_{1-x}$(Al$_2$O$_3$)$_y$(Fe$_2$O$_3$)$_{1-y}$ [17]. The most black pigment ($L^* = 23.5$) has Vis-NIR reflectance of 18.0%.

It can be realized from the previous studies that the pigments with high blackness can be synthesized, however further study should be investigated to enhance their NIR reflectivity. Herein, we report the synthesis of high NIR-reflective Co-doped ZnFe$_2$O$_4$ black pigment with high blackness ($L^* < 30$) and high reflectance ($R > 40\%$). Effects of adding foreign oxides, including CoO$_4$ and PrO$_{11}$ during solid-state reaction on the pigment’s properties are investigated.

2. Experimental procedure
ZnFe$_2$O$_4$ pigment was synthesized by solid-state reaction of ZnO (Cernic International Co., Ltd.) and Fe$_2$O$_3$ (NIC Interchem Co.Ltd.). Stoichiometric amount of ZnO and Fe$_2$O$_3$ were homogeneously mixed by wet ball milling. The mixture was calcined in an electrical furnace under ambient atmosphere at 1000 and 1100 °C for 3 h. The resultant products were washed with de-ionized water for 3 times, dried at 105°C, ground into fine powder and finally sieved through a 325-mesh. Effects of adding foreign oxides, i.e. Co$_3$O$_4$ and Pr$_{4O_{11}}$, were investigated by adding 3 to 30 wt.% Co$_3$O$_4$ (Sigma aldrich) or Pr$_{4O_{11}}$ (C.K. Ceramics) (Sigma aldrich) into the raw material mixture, and synthesized with the same method.

X-ray diffraction analysis was performed on the Rigaku TTRAX III for phase identification. Diffused reflectance spectra were acquired on a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) in the wavelength range of 300 to 2500 nm. The NIR reflectance was calculated in the wavelength range of 700 to 2500 nm following the ASTM standard (number E903-96). The CIE 1976 $L^*$ $a^*$ $b^*$ colorimetric method was employed for color measurement using the Spectrophotometer (Konica Minolta, CM-2600d). In this method, the $L^*$ axis represents the lightness (0 = absolute black, 100 = absolute white), the $a^*$ axis represents the green (negative value) to red (positive value), and the $b^*$ axis represents the blue (negative value) to yellow (positive value).

3. Results and discussion
Figure 1 shows XRD patterns of the undoped samples synthesized by calcination of the ZnO and Fe$_2$O$_3$ at 1000 and 1100°C for 3 h. The undoped samples show strong reflection peaks which can be well matched with the standard pattern of face-centered-cubic ZnFe$_2$O$_4$ with a spinel structure (JCPDF file# 22-1012). The reflection peaks of ZnFe$_2$O$_4$ are sharp and more intense after calcination at higher
temperature (1100 °C) due to an increase of crystallinity. No other peaks of minor phase or impurity are observed.

**Figure 1.** XRD patterns of the undoped samples before and after calcination at 1000 and 1100 °C for 3 h.

**Figure 2.** XRD patterns of the Co-doped samples calcined at (a) 1000 and (b) 1100 °C for 3 h at various Co doping levels.

Figure 2 shows expanded XRD patterns (for (422), (511) and (440) planes) of Co-doped samples after calcination at 1000 and 1100 °C. It reveals that the addition of Co into the ZnFe2O4 did not change its crystal structure. However, doping with Co resulted in a gradual shift of XRD peaks towards higher diffraction angles upon the increased Co content compared to that of the parent phase to form the Co-doped compound, Zn_{1-x}Co_{x}Fe_{2}O_{4}. The XRD peak shift can be ascribed to substitution of a smaller Co^{2+} (ionic radius = 0.58 Å [18]) for a larger Zn^{2+} (ionic radius = 0.60 Å [18]) in tetrahedron site of the spinel structure. Such ionic substitution would lead to a reduction of interplanar spacing, and thus a shift towards higher 2θ value. The peak shift increases with the increase of Co doping level. At 30.1 wt.% doping, the maximum doping level employed in this study, the XRD patterns well match with the pattern of CoFe2O4 phase as a result of complete substitution of Zn^{2+} by Co^{2+} at high doping level. A similar shift of XRD peaks towards higher 2θ value was observed in the substitution of smaller Mg^{2+} for Zn^{2+} in the Mg-doped ZnFe2O4 [16]. However, only a slight shift was observed in this system, and it appears that the extent of peak shifting does not increase with the Mg doping content. It could be possible that Mg doping became saturated at low doping level. In our study, the Zn^{2+} may be gradually substituted by Co^{2+} to completion, forming CoFe2O4. Further study on Mo doping into the ZnFe2O4 is being conducted by Extended X-ray Absorption Fine Structure (EXAFS) analysis.
UV-Vis diffused reflectance spectra of the undoped and Co-doped ZnFe$_2$O$_4$ synthesized at 1000 and 1100 °C are shown in figure 3. The spectra of the undoped samples show two broad absorption bands at around 770 and 1200 nm, a typical characteristics of the zinc ferrite, which are attributed to $^6A_{1g} \rightarrow ^4T_{2g}$ and $^6A_{1g} \rightarrow ^4T_{1g}$ for d-d electron transition of Fe$^{3+}$ [19]. This undoped samples synthesized at 1000 and 1100 °C have NIR reflectance of 65.9 and 61.2%, respectively. The incorporation of Co into ZnFe$_2$O$_4$ resulted in a reduction of NIR reflectance and a change of color hue from light brown to dark brown and finally to black, depending on the amount of the Co doping level as summarized in table 1. In addition, the absorption bands at around 770 and 1200 nm are gradually diminished. In general, upon the increase of Co doping level, the $L^*$ value and reflectance gradually decrease due to a darker color hue. For example, the NIR reflectance decreases from 65.9% for the undoped sample to 44.9% for the sample doped with 16.7 wt.% Co$_3$O$_4$ after calcination at 1000 °C. Higher doping level results in

![Figure 3](image-url)

**Figure 3.** Diffused reflectance spectra of the Co-doped samples calcined at (a) 1000 and (b) 1100 °C for 3 h at various Co doping levels.

**Table 1.** Properties of NIR-reflective ZnFe$_2$O$_4$ pigments doped with Co$_3$O$_4$ before and after calcination at 1000 and 1100 °C for 3 h.

| Co$_3$O$_4$ (wt.%) | Calcined at 1000 °C | Calcined at 1100 °C |
|-------------------|---------------------|---------------------|
|                   | Color coordinate    | Photograph | $R$ (%) | Color coordinate  | Photograph | $R$ (%) |
|                   | $L^*$   | $a^*$  | $b^*$  |       | $L^*$   | $a^*$  | $b^*$  |       |
| 0                 | 49.6    | 25.3   | 35.5   | 65.9  | 47.9    | 27.2   | 37.5   | 61.2  |
| 3.3               | 34.6    | 11.8   | 13.5   | 55.4  | 32.6    | 12.1   | 14.0   | 52.8  |
| 10.0              | 25.5    | 3.9    | 2.1    | 48.7  | 26.2    | 4.2    | 2.4    | 43.8  |
| 16.7              | 25.6    | 1.6    | 0.1    | 44.9  | 25.7    | 1.6    | 0.1    | 42.8  |
| 23.4              | 26.5    | 0.5    | -0.7   | 44.0  | 26.6    | 0.6    | -0.5   | 39.8  |
| 30.1              | 26.0    | 0.5    | -0.8   | 39.5  | 26.8    | 0.3    | -0.8   | 38.4  |
only a slight reduction of $L^*$ and reflectance. Thus, no dramatic change of the color hue at Co content higher than 16.7 wt.%. In addition, calcination at 1000 and 1100 °C had no dramatic effect on the NIR reflectance and color hue of the resultant pigments. Note that values of $a^*$ and $b^*$ dramatically decrease from $>25$ for the undoped samples to approximately 0 for the samples doped with 16.7 wt.% Co or higher, indicating very high black color hue of these pigments. Under the optimum synthesis condition, i.e. 1000 °C and 16.7 wt.% doping, the pigment possesses NIR reflectance of 44.9% and $L^*$ value of 25.56. It can be regarded that the pigment synthesized in this work is high in both darkness and reflectance in comparison to the previous works [15-17].

To further investigate the effect of adding foreign oxide into the zinc ferrite, various amount of Pr$_6$O$_{11}$ was added to the raw material before subjecting to calcination in the same condition as the Co$_3$O$_4$ doping. Figure 4 shows XRD patterns of the samples after calcination at 1100 °C. XRD pattern of the undoped sample well matches with the pattern of ZnFe$_2$O$_4$ without other reflection peaks of impurity. When the Pr$_6$O$_{11}$ was added to the raw material, the calcined product consists of ZnFe$_2$O$_4$, PrFe$_2$O$_3$, as well as unreacted Fe$_2$O$_3$. Upon increasing the Pr$_6$O$_{11}$ content, reflection peaks of the ZnFe$_2$O$_4$ decreases while those of the PrFe$_2$O$_3$ increases. This result indicates that Pr$_6$O$_{11}$ reacts with Fe$_2$O$_3$ during calcination forming PrFe$_2$O$_3$ compound. It is a competing reaction to the ZnO-Fe$_2$O$_3$. The products are composite pigments of ZnFe$_2$O$_4$, PrFe$_2$O$_3$ and Fe$_2$O$_3$.

![Figure 4. XRD patterns of the NIR-reflective pigments consisting various amount of Pr$_6$O$_{11}$ in raw material after calcination at 1100 °C for 3 h.](image)

Figure 5 shows UV-Vis diffused reflectance spectra of the composite pigments. In general, their spectra have similar trend with the spectra of the Co-doped ZnFe$_2$O$_4$ described earlier. That is, the reflectance decreases with the increased proportion of Pr$_6$O$_{11}$ in the raw material. However, the characteristics absorption bands of zinc ferrite at around 770 and 1200 nm slightly decreases with the increased amount of the Pr$_6$O$_{11}$ but they did not disappear as observed in the case of Co-doped ZnFe$_2$O$_4$. Such a slight decreased absorption is attributed to the decreased proportion of ZnFe$_2$O$_4$ in the composite pigment. The NIR reflectance and $L^*$ value gradually decrease from 61.2% and 47.93, respectively, for pure ZnFe$_2$O$_4$ to 48.1% and 39.59, respectively, for the composite pigment synthesized by adding 30 wt.% Pr$_6$O$_{11}$ in the raw material as summarized in table 2. Thus, it is obvious that no doping effect was observed in this case primarily due to its large ionic radius of 0.99 Å (Pr$^{3+}$) [18]. The composite pigment has dark brown color hue with $L^*$ around 40 ±1 and NIR reflectance in a range of 48-50% which is approximately in the same order with the Al-doped CoCr$_2$O$_4$ [15] and Mg-doped ZnFe$_2$O$_4$ [16].
Table 2. Properties of NIR-reflective pigments consisting various amount of Pr$_6$O$_{11}$ in raw material after calcination at 1100 °C for 3 h.

| Pr$_6$O$_{11}$ (wt.%) | Color coordinate | Photograph | R (%) |
|-----------------------|------------------|------------|-------|
|                       | $L^*$ | $a^*$ | $b^*$ |       |
| 0                     | 47.9  | 27.2  | 37.5  | 61.2  |
| 5                     | 39.7  | 26.1  | 25.9  | 60.1  |
| 10                    | 40.5  | 25.1  | 26.6  | 58.0  |
| 15                    | 39.8  | 23.9  | 25.2  | 56.8  |
| 20                    | 41.3  | 22.2  | 25.2  | 52.4  |
| 30                    | 39.6  | 18.0  | 22.2  | 48.1  |

Figure 5. Diffused reflectance spectra of the NIR-reflective pigments consisting various amount of Pr$_6$O$_{11}$ in raw material after calcination at 1100 °C for 3 h.

4. Conclusions
The NIR-reflective Co-doped ZnFe$_2$O$_4$ black pigment with high darkness ($L^* = 25.56$) and NIR reflectance ($R = 44.9\%$) was synthesized by solid-state reaction of ZnO and Fe$_2$O$_3$ at 1000°C in the presence of 16.7 wt.% Co$_3$O$_4$ dopant. A series of black pigments with a gradual increase of blackness and decrease of reflectance can be synthesized by the addition of 3-30 wt.% Co$_3$O$_4$ dopant into the parent ZnFe$_2$O$_4$. The pigments synthesized at 1100°C had comparable black color hue, but had slightly lower NIR reflectance. The black pigments synthesized in this work are high in both blackness and NIR reflectance in comparison to the previous studies. Addition of the Pr$_6$O$_{11}$ to the raw material in place of the Co$_3$O$_4$ had no doping effect, and thus did not dramatically alter the color hue and NIR
reflectance. A composite pigment consisting of ZnFe$_2$O$_4$, PrFe$_2$O$_3$ and unreacted Fe$_2$O$_3$ with $L^*$ value around 40 ±1 and NIR reflectance in a range of 48-50% was obtained.

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