Novel environment-friendly green pigments based on rare earth cuprate

CrossMark

Toshiyuki Masui, Naoki Takeuchi, Hiroki Nakado, Nobuhito Imanaka[*]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

ABSTRACT

Novel green pigments based on $(R_{1-x}R'_x)_2Cu_2O_5$ ($R = Y^{3+}$, $R' = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) solid solutions were synthesized and the dopant concentration was optimized. Among the samples, it was found that $Su_2Cu_2O_5$ based samples showed brilliant green hue. In response to the results, $Sc_2(Cu_{1-x}Zn_x)_2O_5$ ($0 \leq x \leq 0.1$) pigments were further synthesized and their color properties were characterized in an attempt to find a new environmentally friendly pigment that has more sufficient green chromaticity. Among the samples, the most vivid green hue was obtained for $Sc_2(Cu_{0.92}Zn_{0.08})_2O_5$ with a greenness value ($-a^*$) of 41.2 in the CIE $L^*a^*b^*$ system, which was significantly larger than those of commercially available Cr_2O_3 ($-a^* = 18.2$), $CoO \cdot ZnO$ ($-a^* = 25.3$), and Co_2TiO_4 ($-a^* = 35.2$) pigments. Scandium, copper, and zinc in $Sc_2(Cu_{0.92}Zn_{0.08})_2O_5$ are nontoxic elements; therefore, the pigment should be an effective alternative to the conventional toxic green pigments.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Inorganic green pigments are typically applied ceramic tiles, inks, and paints. Green color is associated with natural color of trees and has sedating and relaxing effects to ease tension. However, several conventional industrial pigments such as chrome oxide green (Cr_2O_3), cobalt green ($CoO \cdot ZnO$), and cobalt titanate green spinel (Co_2TiO_4) have serious problems from a practical viewpoint: Cr_2O_3 contains toxic Cr, which have adverse effects on the human body and the environment, and $CoO \cdot ZnO$ and Co_2TiO_4 are less than perfect in green color [1].

In this study, we focused on $Y_2Cu_2O_5$ as a novel environmentally friendly green pigment. This compound adopts an orthorhombic structure (space group: $Pna2_1$), which can be described in terms of one-dimensional Cu_2O_5 chains lying along the a-axis and yttrium ions occupy octahedral sites between these chains [2,3]. The coordination geometry about the copper ions has a distorted square planar form, while the yttrium ions are surrounded by six oxygen atoms arranged in the configuration of a distorted octahedron [4]. As a result, spin-allowed d–d transitions of Cu^{2+} are available, and a part of the visible light was absorbed by these transitions to give green color. In fact, an $Y_2Cu_2O_5$ single crystal has bright green as

reported by our laboratory [5] and bluish-green color was also observed for a powder sample [6].

Generally, the d–d transitions in transition metal ions are strongly affected by the steric structure of the component unit. The transition probability usually increases when the Cu_2O_5 chains are highly asymmetric. Accordingly, it will be possible to control the light absorption wavelength by adjusting the length between Cu^{2+} and O^{2-} to modify the symmetry around the Cu^{2+} ion: it can be expected that the green color becomes more vivid by doping another ion into the $Y_2Cu_2O_5$ lattice to cause a conformational change of the Cu_2O_5 chains.

In this study, therefore, novel green pigments based on $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) solid solutions were synthesized and the composition was optimized for the sample that showed the most vivid color. In response to the results, furthermore, $Sc_2(Cu_{1-x}Zn_x)_2O_5$ ($0 \leq x \leq 0.1$) pigments were synthesized and their color properties were characterized in an attempt to find a new environmentally friendly pigment that has sufficient green chromaticity.

2. Experimental

2.1. Materials

The $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}), $(Y_{1-x}Sc_x)_2Cu_2O_5$ ($0 \leq x \leq 1$), and $Sc_2(Cu_{1-x}Zn_x)_2O_5$ ($0 \leq x \leq 0.1$) pigments were synthesized using a conventional solid state

* Corresponding author.
    E-mail address: imanaka@chem.eng.osaka-u.ac.jp (N. Imanaka).

reaction method. Stoichiometric amounts of Y_2O_3, R_2O_3, and CuO powders were mixed in an agate mortar, followed by mechanically mixing using a planetary-type ball-milling apparatus (Pulverisette 7, Fritsch GmbH) for 3 h. The homogenous mixed powder was calcined at 1373 K for $(Y_{0.9}R_{0.1})_2Cu_2O_5$ and $(Y_{1-x}Sc_x)_2Cu_2O_5$ or at 1273 K for $Sc_2(Cu_{1-x}Zn_x)_2O_5$ for 12 h under an air atmosphere. Before characterization, the samples were gently ground in an agate mortar.

2.2. Characterization

X-ray fluorescence spectroscopy (XRF; Rigaku, ZSX-100e) measurements indicated the sample compositions were in good agreement with the nominal stoichiometric compositions of the starting mixtures. The pigments were characterized by X-ray powder diffraction (XRD; Rigaku, SmartLab) with Cu Kα radiation (40 kV and 30 mA). The lattice parameters and volumes of the samples were calculated from the XRD peak angles, which were refined using α-Al_2O_3 as a standard. Particle morphology was examined by scanning electron microscopy (SEM; Shimadzu, SS-550). The size distribution and mean particle size were estimated by measuring the diameters of 200 particles from SEM micrographs.

The optical reflectance was measured using a UV–vis spectrometer (Shimadzu, UV-2600) with barium sulfate as a reference. The bandgap energies of the samples were determined from the absorption edge of the absorbance spectra represented by the Kubelka–Munk function, $f(R) = (1 - R)^2/2R$, where R is reflectance [7].

The color properties of the green pellets of the samples were estimated in terms of the CIE $L^*a^*b^*$ system with a colorimeter (Konika-Minolta, CR-400). The parameter L^* represents the brightness or darkness of a color relative to a neutral gray scale, while the parameters a^* (the red–green axis) and b^* (the yellow-–blue axis) qualitatively express the color. Since the a^* value in the negative direction corresponds to the green component, it is desirable for a^* to be small (for $-a^*$ to be large) as possible on the development of green pigments. The parameter C (chroma) represents saturation of the color and $H°$ represents the hue angle. The chroma is defined as $C = \{(a^*)^2 + (b^*)^2\}^{1/2}$. The hue angle, $H°$, is expressed in degrees and ranges from 0 to 360° and is calculated using the formula $H° = \tan^{-1}(b^*/a^*)$. For pure green, $H° = 180°$.

A light resistance test under UV irradiation was also performed using a UV lamp (Toshiba, EFD15BLB), of which the emission peak wavelength was 352 nm, to evaluate the light stability of the pigment color. The color difference of the pigment after exposure to the UV irradiation for 170 h was evaluated using the colorimeter.

3. Results and discussion

3.1. $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+})

Fig. 1 shows XRD patterns of the $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}) samples. A single-phase orthorhombic structure was observed for all samples, and no diffraction peaks of impurities were evident in the patterns. The XRD peaks shifted to higher angle direction with increasing the R content expect Gd^{3+}, because Y^{3+} (ionic radius: 0.0900 nm) [8] in the host lattice is partially substituted by smaller Sc^{3+} (0.0745 nm) [8], Tm^{3+} (0.0880 nm) [8], Yb^{3+} (0.0868 nm) [8], and Lu^{3+} (0.0861 nm) [8] ions. On the other hand, the peak shifted to lower angle direction with increasing the Gd content due to larger ionic radius of Gd^{3+} (0.0938 nm) [8]. The orthorhombic lattice volumes of the $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+},
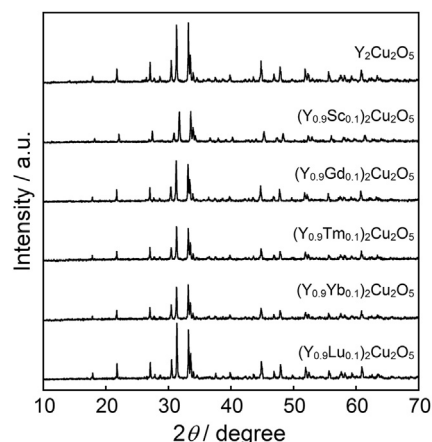

Fig. 1. XRD patterns of $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}).

and Lu^{3+}) samples calculated from the diffraction angles in the XRD patterns are summarized in Table 1. The lattice volume of the orthorhombic phase depends on the ionic radius of the doped rare earth ion, indicating the formation of solid solutions.

Fig. 2 depicts UV–vis diffuse reflectance spectra for the $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ samples. All samples exhibited strong optical absorption at wavelengths shorter than 400 nm and longer than 600 nm. As a result, strong reflection was recognized only at wavelengths between 400 and 600 nm including the green region (500–560 nm) and the samples are green. The optical absorption shorter than 400 nm is attributed to the charge transfer transition from O^{2-} to Cu^{2+}, while that longer than 600 nm corresponds to the d–d transitions of Cu^{2+} [6,9,10]. The absorption intensity was dependent on the rare earth content. The $(Y_{0.9}Sc_{0.1})_2Cu_2O_5$ sample exhibited the highest absorption in the red light region (600–750 nm). As a result, the highly-colored green was observed for this sample, because red is the complementary color of green.

The $L^*a^*b^*C$ $H°$ color coordinate data for the $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ pigments are summarized in Table 2. The L^*, a^*, b^*, C, and $H°$ values are dependent on the sample composition. The $(Y_{0.9}Sc_{0.1})_2Cu_2O_5$ sample has the highest $-a^*$ value (13.2). Consequently, the $(Y_{0.9}Sc_{0.1})_2Cu_2O_5$ pigment has the most greenish hue among the $(Y_{0.9}R_{0.1})_2Cu_2O_5$ samples. However, the $-a^*$ and C values were too small to be available for a green pigment. Also, the color purity was not enough because the $H°$ value of 217° corresponds to not blue but blue-green.

3.2. $(Y_{1-x}Sc_x)_2Cu_2O_5$ ($0 \leq x \leq 1$)

In response to the results of the previous section, $(Y_{1-x}Sc_x)_2Cu_2O_5$ ($0 \leq x \leq 1$) samples were then synthesized. Fig. 3 shows XRD patterns of them. For $0 \leq x \leq 0.6$, a single-phase orthorhombic $Y_2Cu_2O_5$-type structure (space group: $Pna2_1$) [2] was observed, while that of similar orthorhombic $Sc_2Cu_2O_5$-type

Table 1
Lattice volumes of $Y_2Cu_2O_5$ and $(Y_{0.9}R_{0.1})_2Cu_2O_5$ ($R = Sc^{3+}$, Gd^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}).

Sample	Lattice volume/nm^3
$Y_2Cu_2O_5$	0.4698
$(Y_{0.9}Sc_{0.1})_2Cu_2O_5$	0.4687
$(Y_{0.9}Gd_{0.1})_2Cu_2O_5$	0.4706
$(Y_{0.9}Tm_{0.1})_2Cu_2O_5$	0.4694
$(Y_{0.9}Yb_{0.1})_2Cu_2O_5$	0.4692
$(Y_{0.9}Lu_{0.1})_2Cu_2O_5$	0.4690