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Novel Environment-friendly Green Pigments for Over-glazed Decoration of *Arita* Ware

Toshiyuki MASUI*, Atsunori SHIRAISHI**, Hiroki NAKADO*, Naoki TAKEUCHI*, WENDUSU* and Nobuhito IMANAKA*,†

* *Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*
** *Saga Ceramics Research Laboratory, 3037-7 Kuromuta-hei, Arita-cho, Nishimatuura-gun, Saga 844-0022, Japan*
†*Corresponding Author, E-mail: imanaka@chem.eng.osaka-u.ac.jp*

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Abstract

Environmental-friendly inorganic green pigments based on $(Y_{0.9}R_{0.1})_2BaCuO_5$ (R = Sm^{3+}, Gd^{3+}, Yb^{3+}, and Lu^{3+}) solid solutions were synthesized and the dopant element was optimized to give the most greenish color. Among the samples, it was found that Lu-doped sample showed brilliant green hue. In response to the results, $(Y_{1-x}Lu_x)_2BaCuO_5$ ($0 \leq x \leq 0.3$) 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 $(Y_{0.9}Lu_{0.1})_2BaCuO_5$ with a greenness value ($-a^*$) of 48.6 in the CIE $L^*a^*b^*$ system, which was significantly larger than those of commercially available Cr_2O_3 ($-a^*$ = 18.2) and CoO·ZnO ($-a^*$ = 25.3) pigments. The Y_2BaCuO_5 and $(Y_{0.9}Lu_{0.1})_2BaCuO_5$ pigments were used in paints for porcelain. The green colors of the overglazed decoration panels were brilliant. Therefore, these pigments could be the potential candidates for novel green pigments of over-glazed decoration of *Arita* ware.

Key-words: *Y_2BaCuO_5, Environment-friendly, Green pigment, Solid solution, Arita ware*

1. Introduction

Inorganic green pigments are typically applied to ceramic tiles, inks, and paints. Chrome oxide green (Cr_2O_3) and cobalt green (CoO·ZnO) have been known as conventional materials[1)], but they have serious problems from a practical viewpoint. They are less than perfect in green color, and, in particular, Cr_2O_3 is of concern due to the toxicity of Cr which has adverse effects on the human body and the environment.

In this study, we focused on Y_2BaCuO_5 as an environmentally friendly green pigment. This compound adopts an orthorhombic structure (space group: *Pbnm*), which are composed of CuO_5, Y_2O_{11}, and BaO_{11} polyhedra[2-5)]. The coordination geometry around the copper ions is a distorted square-pyramid form. 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[5,6)].

Generally, the d-d transitions are strongly affected by the steric structure of the component unit, and the transition probability usually increases when the coordination geometry around the transition metal ions is highly asymmetric. The crystal field effect to split the d orbitals depends on the length between Cu^{2+} and O^{2-} in Y_2BaCuO_5. Accordingly, it should be possible to control the light absorption strength and wavelength by modifying the CuO_5 polyhedra: it can be expected that the green color becomes more vivid by doping another ion into the Y_2BaCuO_5 lattice to cause a conformational change of the CuO_5 polyhedra.

In this study, therefore, novel green pigments based on $(Y_{0.9}R_{0.1})_2BaCuO_5$ (R = Sm^{3+}, Gd^{3+}, Yb^{3+}, and Lu^{3+}) solid solutions were synthesized and the composition was optimized for the sample that showed the most vivid green color. In response to the results, furthermore, the potential of the $(Y_{0.9}Lu_{0.1})_2BaCuO_5$ and Y_2BaCuO_5 pigments were evaluated as a new environmentally friendly green pigment for *Arita* ware.

2. Experimental

2.1 Materials

The Y_2BaCuO_5, $(Y_{0.9}R_{0.1})_2BaCuO_5$ (R = Sm^{3+}, Gd^{3+}, Yb^{3+}, and Lu^{3+}), and $(Y_{1-x}Lu_x)_2BaCuO_5$ ($0.05 \leq x \leq 0.3$) pigments were synthesized using a conventional solid state reaction method. Stoichiometric amounts of Y_2O_3, R_2O_3, CuO, and $BaCO_3$ powders were mixed in an agate mortar, and the homogenous mixed powder was calcined twice at 1273 K 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; Shimadzu, EDX-720) measurements indicated the sample compositions were in good agreement with theoretical values. The pigments were characterized by X-ray powder diffraction (XRD; Rigaku, SmartLab) with Cu Kα radiation (40 kV and 30 mA). The lattice volumes of the samples were calculated from