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Novel Lead-free CeO_2-ZrO_2-Bi_2O_3 Yellow Pigments for Arita Ware

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Abstract

CeO_2-ZrO_2-Bi_2O_3 yellow pigments were prepared by a citrate complex method and their color properties were characterized to evaluate their suitability as environmentally friendly inorganic pigments. CeO_2-ZrO_2-Bi_2O_3 yellow pigments strongly absorb visible light at wavelengths below 500 nm and consequently they are brilliant yellow in color. The most vivid yellow was obtained for $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.90}$, which had a yellowness value (b^*) in the CIE $L^*a^*b^*$ system comparable to that of the commercially available praseodymium yellow pigment ($ZrSiO_4$:Pr). The $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.90}$ pigment was used in paints for porcelain. We found that the medium yellow pigment (*chuuki*), which is one of the traditional colors of *Arita* ware but which contains lead and antimony, could be faithfully replicated without using these toxic elements.

Key-words: *CeO_2-ZrO_2-Bi_2O_3, Solid solution, Environmentally friendly, Yellow pigment, Arita ware*

1. Introduction

Ceramic businesses in Saga prefecture in Japan are under pressure due to competition from imported products from other countries as well as similar products produced in other prefectures in Japan. It is thus important to achieve product differentiation to produce unique products. Vividly colored overglazed products, a distinctive class of ceramics known as *Arita* ware, are unique to Saga. The same pigments have been used in overglazing for many years. There is thus a strong demand to develop new pigments.

There are two kinds of traditional yellow pigments used in the overglazing of *Arita* ware: a slightly brownish yellow pigment with a high transparency known as *kibi-iro* and reddish yellow pigments with high chromatic contrasts known as *koiki*, *chuuki*, and *usuki*. The coloration of the latter pigments is derived from lead, iron, and antimony. Praseodymium yellow ($ZrSiO_4$:Pr)[1] has been used as a lead-free substitute for these pigments. However, praseodymium yellow is slightly bluish (it is lemon yellow) compared with *koiki*, *chuuki*, and *usuki* and it has a different tone from these traditional pigments even when color matching is performed using other paints. Therefore, a novel lead-free pigment that can replicate the colors of *koiki*, *chuuki*, and *usuki* is required by potteries that place a premium on traditional colors.

We have been working to synthesize several lead-free pigments for porcelain to satisfy the demands of environment- and safety-oriented consumers. This is also important in a general way because several conventional industrial pigments such as chrome yellow ($PbCrO_4$), cadmium yellow (CdS), and cadmium red (CdS/CdSe) contain toxic elements such as Pb, Cr, Cd, and Se and no potential substitutes for these pigments have been found[2]. In this study, novel environmental-friendly pigments based on CeO_2-ZrO_2-Bi_2O_3 solid solutions ($Ce_{1-x-y}Zr_xBi_yO_{2-y/2}$) have been synthesized to search for a new lead-free yellow pigment for *Arita* ware. The coloring mechanism of these CeO_2-ZrO_2-Bi_2O_3 materials is based on charge transfer transition from O_{2p} to Ce_{4f} in the CeO_2 band structure[3-6]. Doping Bi^{3+} in the CeO_2-ZrO_2 lattice generates intrinsic strain, which alters the O_{2p} valence band and reduces the band-gap energy due to the formation of a hybrid Bi_{6s} and O_{2p} orbital[7]. The composition of these pigments has been optimized and their color properties have been found to be suitable for *Arita* ware.

2. Experimental

2.1 Materials

CeO_2-ZrO_2-Bi_2O_3 pigments were synthesized by cation complexation using citric acid. A stoichiometric mixture of 1 mol L^{-1} $Ce(NO_3)_3$, 1 mol L^{-1} $ZrO(NO_3)_2$, and 0.5 mol L^{-1} $Bi(NO_3)_3$ aqueous solutions was mixed with a 1 mol L^{-1} citric acid solution. The molar Ce:Zr ratio was kept constant at 55:45 to give the deepest yellow hue[3] while the molar ratio of bismuth was increased from 0 to 23 mol%. After stirring at 353 K for 5 h, the solvent was evaporated at 353 K using a rotary evaporator. The solid obtained was dried at 403 K for 1 h and successively calcined at 1273 K for 1 h.

2.2 Characterization

The pigments were characterized by X-ray powder diffraction (XRD; Rigaku, SmartLab) with Cu-Ka radiation (40 kV and 30 mA). Rietveld refinement of the XRD patterns was performed