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Novel Environment-Friendly Blue Pigments Based on $Ba(TiO)Cu_4(PO_4)_4$

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Abstract

The novel environment-friendly blue pigments $Ba(TiO)(Cu_{1-x}Li_x)_4(PO_4)_4$ ($0 \le x \le 0.15$), have been synthesized and their color properties investigated. By doping Li into the Cu sites, which causes distortion of the CuO_4 units, overlap of the charge transfer and *d-d* transition absorption bands has been successfully controlled. Among the samples, $Ba(TiO)(Cu_{0.90}Li_{0.10})_4(PO_4)_4$ showed the most vivid blue hue, with a blueness value ($-b^*$) of 57.6, a value comparable with that of the commercially available $CoAl_2O_4$ pigment (cobalt blue, $-b^* = 59.5$). Moreover, the hue angle of this sample ($H° = 268.7°$) is close to the pure-blue hue angle ($H° = 270°$).

Key-words: *$Ba(TiO)Cu_4(PO_4)_4$, Inorganic blue pigment, Environment-friendly, Solid solution, Divalent Copper ion*

1. Introduction

Because inorganic pigments have high thermal and chemical durability with high hiding power compared to that of organic pigments, they are widely used in paints, glazes, and inks that are required to maintain their color for long periods. Today, while various kinds of inorganic pigments are commercially available, most of them contain toxic heavy metals such as Cr, Co, Cd, and Pb, because these provide the basis for their strong and brilliant hues. However, the use of such heavy metals is becoming restricted, and it is therefore desirable to develop alternative inorganic pigments that do not contain toxic heavy metals. Among the colors, blue is one of the three primary colors (together with red and yellow), and this gives rise to a strong demand for blue pigments. Cobalt compounds such as Co_2SiO_4, $CoAl_2O_4$, Co_2SnO_4, and $(Co,Zn)_2SiO_4$ are well known as commercially useful blue pigments because the Co^{2+} ion incorporated in these compounds gives them a vivid blue hue[1]. However, as mentioned above, since Co^{2+} and its compounds are harmful to the human body and the environment, they have been designated as hazardous substances under the PRTR (pollutant release and transfer register) system, and their use has been restricted in recent years[1]. Although some compounds with reduced Co^{2+} ion content have been proposed, with the aim of lowering the adverse effects of the Co^{2+} ion[2-4], these pigments still contain a certain level of Co^{2+}, and thus do not meet the requirements for higher safety. One dark blue inorganic pigment that does not contain harmful Co^{2+} is the compound $Fe^{III}_4[Fe^{II}(CN)_6]$, the blue color of which arises from the fact that it absorbs yellow light due to charge transfer between Fe^{2+} and Fe^{3+}. It has disadvantages, however, in the low vividness of its blue color, and its poor thermal stability, with decomposition to iron oxide gradually occurring above 140 °C.

One source of blue color is the *d-d* transition of Cu^{2+} in square planar or square pyramidal coordination, which gives rise to absorption of visible light in the yellow to red spectral region, and thus causes the compound to exhibit a blue to green color[5]. We have therefore focused on $Ba(TiO)Cu_4(PO_4)_4$ as the mother crystal of a new blue inorganic pigment, composed solely of elements harmless to the human body and the environment, and containing square planar CuO_4 units in its structure[6]. Furthermore, the color of $Ba(TiO)Cu_4(PO_4)_4$ can be improved by controlling the charge transfer and *d-d* transition of the metal ion, because these are generally influenced by both the crystal structure and the coordination environment of the metal ions, which are easily controlled by partial substitution of the metal sites in $Ba(TiO)Cu_4(PO_4)_4$ by other ions having different ionic radii or valence states.

In this study, we partially replaced the Cu^{2+} ions (radius 0.057 nm, coordination number CN = 4)[7] in the metal sites of $Ba(TiO)Cu_4(PO_4)_4$ with the larger Li^+ ions (radius 0.059 nm, CN = 4)[7] in order to intentionally distort the CuO_4 units in the structure and thereby cause a shift of the absorption bands due to charge transfer and *d-d* transitions, and we investigated the color properties of the products.

2. Experimental

2.1 Materials

$Ba(TiO)(Cu_{1-x}Li_x)_4(PO_4)_4$ solids were prepared by a conventional solid-state reaction method. $BaCO_3$, TiO_2, CuO, Li_2CO_3, and $(NH_4)_2HPO_4$ were mixed using an agate

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