Synthesis of Bi$_2$O$_3$–ZrO$_2$ solid solutions for environment-friendly orange pigments

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Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions were synthesized by conventional ceramic method and their color properties were investigated as environment-friendly inorganic orange pigments. Single phased Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions with tetragonal crystal structure are formed in the range of 0.3 $\leq x \leq$ 0.5 compositions. Brilliant orange color powders were obtained for $x = 0.5$ composition heated at 800°C, which had color parameters ($L^*$, $a^*$, $b^*$) of $L^*$ = 68, $a^*$ = 34, and $b^*$ = 69. The color of $x = 0.5$ samples is comparable to that of orange color specified in Japanese Industrial Standards (JIS) for a traffic paint. Since Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions are composed of nontoxic elements, it should be an alternative candidates to conventional PbCrO$_4$-based pigments for traffic paint.

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1. Introduction

Synthetic inorganic pigments are widely used for various products such as paints, ceramics, glasses, and plastics since they possess high thermal, chemical, and UV-ray stability compared to organic pigments.

At present, PbCrO$_4$-based orange pigments are traditionally used for a traffic paint around the world. However, the use of these pigments containing toxic elements such as Pb and Cr can adversely affect the environment and human health.

Cr$_2$O$_3$–Sb$_2$O$_5$–TiO$_2$ and BiVO$_4$-based pigments are well known as inorganic orange/yellow pigments. These pigments present similar color to that of PbCrO$_4$-based pigments, however, they are not attractive as a replacement for the PbCrO$_4$-based pigments since it also contain toxic and pollutant elements such as Cr, Sb, and V.

For this reason, the main attention has been directed to the synthesis of new inorganic compounds with orange color which can be used as replacement of PbCrO$_4$-based pigments.

As for candidates of environment-friendly orange pigment, Bi$_2$O$_3$-based solid solutions such as Bi$_2$O$_3$–Y$_2$O$_3$, Bi$_2$O$_3$–Y$_2$O$_3$–ZrO$_2$, Bi$_2$O$_3$–Er$_2$O$_3$–ZrO$_2$, and Bi$_2$O$_3$–ZrO$_2$ are reported.

In case of Bi$_2$O$_3$–Y$_2$O$_3$ and Bi$_2$O$_3$–Er$_2$O$_3$–ZrO$_2$ solid solutions, massive expensive raw materials such as Y$_2$O$_3$ and Er$_2$O$_3$ are needed to synthesize these pigments. On the other hand, in case of Bi$_2$O$_3$–ZrO$_2$ solid solutions, it can be synthesized pigment with relatively low cost. As for Bi$_2$O$_3$–ZrO$_2$ solid solutions, Sulcova et al. reported that Bi$_{2-x}$Zr$_{3x/4}$O$_3$ (0 $\leq x \leq$ 1.9) solid solutions show vivid orange color in the compositions around $x = 0.6$. They have reported general color properties of the solid solutions, but detailed color properties according to the compositional change have not been reported. As mentioned above, it is believed that this compound is a promising orange pigment for traffic paint since it do not contain toxic and pollutant elements. Thus, it is important to investigate detailed color properties of this compound. In this study, Bi$_{2-x}$Zr$_{3x/4}$O$_3$ (0 $\leq x \leq$ 1.9) solid solutions have been synthesized to investigate their potential as an environment-friendly orange pigments for traffic paint.

2. Experimental procedure

Bi$_2$O$_3$ (Wako Pure Chemical Industries Ltd., 99.9%) and ZrO$_2$ (Wako Pure Chemical Industries Ltd., 99.0%) powders were used for the synthesis of Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions. These powders were thoroughly mixed in an agate mortar with a pestle for 10 min, then heated at 800°C in air for 60 min (heating rate 200°C/h). After heating, the resulting mixtures were thoroughly milled in agate mortar with pestle for 10 min. Crystal phases of samples were identified by an X-ray diffractometer (Rigaku Denki Co., Ltd., RINT-2550).

In order to test the color performance of the powders as pigments, pastes were prepared by mixing powders and silicone resins (Cemedine Co., Ltd.) with 25 volume percent powders. The resulting pastes were applied to a white hard paper by a die coating method. The thickness of the coated films obtained were approximately 0.2 mm. The color parameters ($L^*$, $a^*$, $b^*$) were measured using a spectrophotometer (Konica Minolta Sensing Inc., CM-700d). The color parameter $L^*$ represents the brightness or darkness of a color relative to a neutral grey scale, while the color parameters $a^*$ (the green-red axis) and $b^*$ (the blue-yellow axis) qualitatively express the color.

3. Results and discussion

According to the phase diagram of Bi$_2$O$_3$–ZrO$_2$ system, the Bi$_2$O$_3$–ZrO$_2$ solid solutions are formed when mixtures of Bi$_2$O$_3$ and ZrO$_2$ powders are heated at 710°C or above. Therefore, mixtures of Bi$_2$O$_3$ and ZrO$_2$ powders were heated at 800°C to credibly synthesize the solid solutions.

Representative XRD patterns of samples are shown in Fig. 1. Analysis of X-ray diffraction patterns confirmed that samples are divided into three regions depending on the compositions. A mixed phases of monoclinic crystal structure of Bi$_2$O$_3$ and tetragonal crystal structure of Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions is observed in the 0 $< x < 0.3$ compositions. In the 0.3 $\leq x < 0.6$ compositions.
compositions, a single phase of tetragonal crystal structure of Bi2–xZr1/4O3 solid solutions is observed. Moreover, mixed phase consists of tetragonal crystal structure of Bi2–xZr1/4O3 solid solutions and monoclinic crystal structure of ZrO2 are observed in the 0.6 ≤ x compositions. With increasing x in the x = 0.6–1.9 samples, the X-ray peak strength of ZrO2 are clearly increased. Thus, it is evident from analysis of X-ray diffraction patterns that a single phase of Bi2–xZr1/4O3 solid solutions is only formed in the range of 0.3 ≤ x ≤ 0.5 compositions. This result is in good agreement with the compositional region reported by Sulcova et al.7)

As described in introduction part, Sulcova et al. have reported general color properties of Bi2–xZr1/4O3 solid solutions, but detailed color properties according to the compositional change around x = 0.1–0.5 composition have not been reported. Thus, the color properties of samples were investigated except for the samples including unreacted ZrO2 particles. The relationship between crystal phase and color parameters (a*, b*) of samples are shown in Fig. 2. The a* and b* values indicate the degree of red and yellow color of the samples, respectively.

Color of x = 0 sample containing none of ZrO2 is a light yellow. It is evident from the figure that a* and b* values of the samples obviously increases in the composition with the tetragonal crystal phase, and are almost constant values for x = 0.4 and 0.5 samples. Therefore, it seems that the formation of tetragonal crystal phase of Bi2–xZr1/4O3 solid solutions is related to the cause of increase of a* and b* values in the samples.

As for Bi2O3 crystal, it is considered that the coloration of Bi2O3 is derived from visible light absorption due to the transition from a valence band of lone electron pair of O2p to a conduction band of O2p–Bi6p hybrid orbital.9) As for Bi2–xZr1/4O3 solid solutions with small amount of ZrO2 content, it seems that the basic coloring mechanism is same mechanism in case of Bi2O3 crystal. Although the details of color change mechanism of the solid solutions have not been clear at this time, it seems that the small change of band-gap energies (Eg) in band structure due to the formation of solid solutions caused the increase of a* and b* values of samples.

Figure 3 offers a representative photograph of powders for Bi2–xZr1/4O3 solid solutions. As can be seen from the figure, these sample show brilliant orange color.

The sample with brilliant orange color was obtained for x = 0.5 composition, which had color parameters (L*, a*, b*) of L* = 68, a* = 34, and b* = 69. Table 1 shows the color parameters (L*, a*, b*) of x = 0.5 sample and typical orange color compounds10) for inorganic pigments.

In Japan, orange color for traffic paint is specified in the Japanese Industrial Standards K5665 (JIS K5665).11) According to the standards, orange color for traffic paint is shown 5.5YR 6.5/12 at the Munsell color system and the color corresponds to L* = ~71, a* = ~32, b* = ~53 in color parameters (L*, a*, b*). Since color parameter of x = 0.5 sample (L* = 68, a* = 34, b* = 69) is similar to the orange color (L* = ~71, a* = ~32, b* = ~53) specified in JIS K5665, Bi2–xZr1/4O3 solid solutions seems to be attractive candidates for an environment-friendly orange pigments.

Regarding on pigments, color stability of pigments under harsh environment such as acid rain and strong UV-ray is essential, not to mention the color. Although Bi2O3-based pigments have been known as an environment-friendly pigment, it is also known that it easily dissolves in a diluted nitric acid solution. It has been reported that acid rain include nitric acid as the one of main components.12) Thus, it is important to evaluate color stability of Bi2–xZr1/4O3 solid solutions to aqueous diluted nitric acid solution. By soaking the x = 0.5 samples in diluted nitric acid solution.
solution (1 mol/L) at room temperature, discoloration of Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions were observed. Figure 4 offers photograph of $x = 0.5$ sample before and after the soaking test.

As can be seen from the figure, the color of $x = 0.5$ sample was changed from orange to white color by soaking in 30 min. This is believed to be due to the elution of Bi$_2$O$_3$ from Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions to nitric acid solution. It seems that white residue is ZrO$_2$ particles since ZrO$_2$ is insoluble to diluted nitric acid solution. It was found from the result that some measures relating to discoloration of powders are necessary when Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions are applied for pigment.

From now on, for example, silica coating of particles will be considered to solve this issue to realize environment-friendly pigments for traffic paint.

4. Conclusions

Bi$_{2-x}$Zr$_{3x/4}$O$_3$ ($0 < x < 1.9$) solid solutions were synthesized to investigate their potential as an environment-friendly orange pigments. Analysis of X-ray diffraction patterns confirmed that the samples are divided into three regions depending on the compositions. A single phase with tetragonal crystal phase of Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions is formed in the $x = 0.3-0.5$ compositions. Brilliant orange color powders were obtained for $x = 0.5$ composition heated at 800°C, which had color parameters ($L^*$, $a^*$, $b^*$) of $L^* = 68$, $a^* = 34$, and $b^* = 69$. The color parameters $a^*$ and $b^*$ values of $x = 0.5$ samples are comparable to that of orange color specified in JIS K5665 for traffic paint. Discoloration of Bi$_{2-x}$Zr$_{3x/4}$O$_3$ solid solutions were observed by soaking the $x = 0.5$ samples in diluted nitric acid solution.

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