

Novel Environment-friendly Yellow Pigments Based on (Bi, La)VO₄

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Bi_{1-x}La_xVO₄ pigments were synthesized as new environment-friendly inorganic materials, and their color properties were characterized. The Bi_{1-x}La_xVO₄ pigments show brilliant yellow colors, and the most effective yellow hue was obtained for Bi_{0.90}La_{0.10}VO₄. Since BiVO₄ has been known as an environment-friendly inorganic yellow pigment and La is also a nontoxic element, the Bi_{0.90}La_{0.10}VO₄ pigment should provide effective alternatives to conventional toxic yellow pigments.

Inorganic pigments have been applied in various products such as paints, ceramics, plastics, enamels, and glasses, because they possess high thermal and UV stability.¹ In particular, inorganic yellow pigments are much in demand due to their utilities in many applications. Cadmium yellow (CdS) and chromium yellow (PbCrO₄) used to be popular inorganic yellow pigments. However, the use of these pigments has been restricted because they contain hazardous elements such as cadmium (Cd), lead (Pb), and chromium (Cr), which are harmful not only to our health but also to the environment. Although praseodymium yellow (ZrSiO₄:Pr)² has been known as an environment-friendly inorganic yellow pigment for ceramics, the coloring power is lacking in comparison with those of conventional toxic pigments. Therefore, a number of studies have been reported on new environment-friendly yellow pigments,³⁻¹³ but unfortunately, novel pigments which can show brilliant yellow color comparable to or higher than those of the conventional toxic ones have not been realized yet.

Because of this situation, we focused on bismuth vanadate (BiVO₄), which is already known to be an environment-friendly inorganic yellow pigment.¹ It is well known that BiVO₄ exists in three polymorphs; tetragonal dreyerite, monoclinic scheelite, and orthorhombic pucherite.¹⁴ Among them, monoclinic BiVO₄ is thermodynamically stable and vivid yellow.¹⁵ The coloring mechanism of monoclinic BiVO₄ results from the charge-transfer transition from the valence band of a hybrid orbital of Bi_{6s} and O_{2p} to the conduction band of V_{3d}.¹⁶ It is expected that the color of the BiVO₄ pigment can be tuned by introducing other elements into the BiVO₄ lattice to control the lattice size, because the extent of the orbital hybridization in the valence band should depend on the interionic distance between Bi³⁺ and O²⁻.

In this study, therefore, a portion of Bi³⁺ ions in the monoclinic BiVO₄ lattice was substituted with La³⁺, which is also a nontoxic element, to enhance the color intensity. Since the ionic radius of La³⁺ (0.116 nm)¹⁷ is smaller than that of Bi³⁺ (0.117 nm),¹⁷ partial substitution of the Bi³⁺ site with La³⁺ results in the shrinkage of the BiVO₄ lattice. Accordingly, the orbital hybridization effect of Bi_{6s} and O_{2p} should be enhanced to decrease the band gap energy between the valence and the conduction bands. As a result, the pigment color is expected to be deep yellow. In the present study, therefore, Bi_{1-x}La_xVO₄

solid solutions were synthesized as new environment-friendly yellow pigments, and their color properties were characterized from the viewpoint of possible ecological inorganic materials.

The Bi_{1-x}La_xVO₄ (0 ≤ x ≤ 0.15) pigments were synthesized by a hydrothermal method.^{18,19} A stoichiometric mixture of aqueous solutions of 0.5 mol dm⁻³ Bi(NO₃)₃ and 0.1 mol dm⁻³ La(NO₃)₃ was added to 30 cm³ of nitric acid solution (3 mol dm⁻³), in which 1.08 g of NH₄VO₃ was dissolved. The pH of the mixture was adjusted to 6 by dropwise addition of aqueous ammonia (5%). After aging at room temperature for 12 h without stirring, the mixed solution was transferred into a Teflon® bottle in a sealed vessel and heated at 443, 473, and 503 K for 72 h in an oven. The resultant solid was separated by centrifuging, washed with deionized water and ethanol three times, and dried at 333 K for 12 h to obtain the product.

The pigments were characterized by X-ray powder diffraction (XRD, Rigaku Multiflex) to identify the crystal structure. Optical reflectance spectra were obtained with a UV-vis spectrometer (Shimadzu UV-2550) using barium sulfate as a reference. The color properties were evaluated in terms of CIE L*a*b* with a chromometer (Konica-Minolta CR-300). The value L* represents the brightness or darkness of the color as related to a neutral gray scale, and the values a* (the axis red-green) and b* (the axis yellow-blue) indicate the color hue.

The XRD patterns of the Bi_{1-x}La_xVO₄ samples synthesized at 473 K are shown in Figure 1. A single phase of monoclinic BiVO₄ structure was observed for the samples in which the La³⁺ content was 10 mol % or less, and there were no extra lines due to other compounds or impurity phases. On the contrary, in the sample that the La³⁺ content was 15 mol %, tetragonal BiVO₄

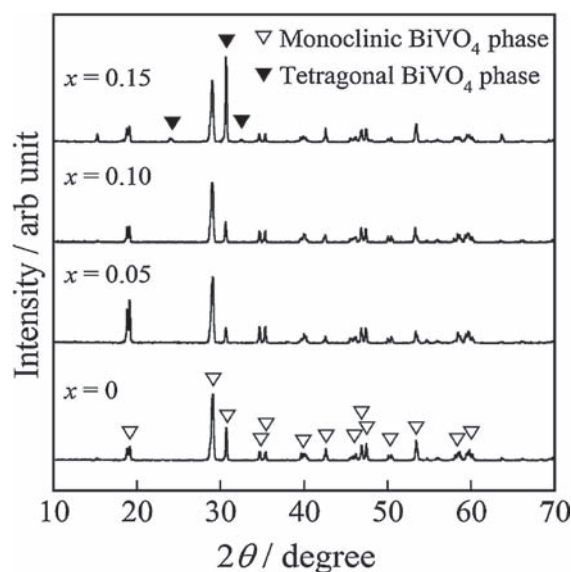


Figure 1. XRD patterns of the Bi_{1-x}La_xVO₄ samples.

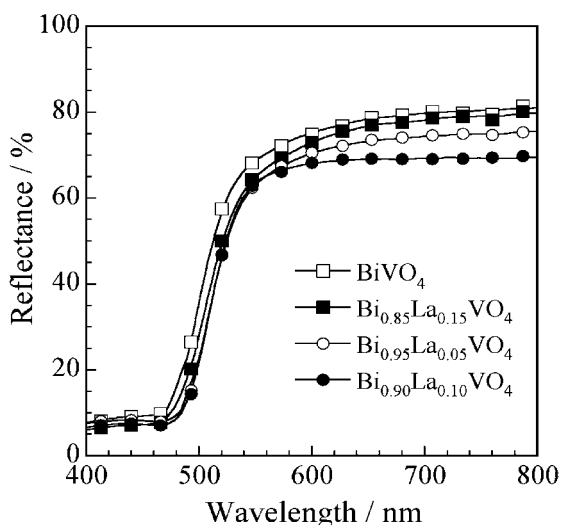


Figure 2. Reflectance spectra of the $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ pigments.

phase was observed as a secondary phase. In the region forming the single monoclinic BiVO_4 structure, the XRD patterns slightly shifted to higher angles by substituting the Bi^{3+} (0.117 nm)¹⁷ site with smaller La^{3+} (0.116 nm)¹⁷ in the lattice (Figure S1 in the Supporting Information; SI).²⁰ The effect of La^{3+} content on the lattice parameters of the $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ samples are also summarized in Table S1 (in the SI).²⁰ The lattice parameters of the samples monotonously decreases with the increase in the amount of La^{3+} in the single phase region ($0 \leq x \leq 0.10$), because ionic radius of La^{3+} (0.116 nm)¹⁷ is smaller than that of Bi^{3+} (0.117 nm).¹⁷ However, the lattice parameters of the sample became approximately constant in the two-phase region. These results imply that the solid solutions of the single monoclinic BiVO_4 phase are successfully formed and that the solubility limit is around $x = 0.10$ in $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$.

Figure 2 depicts the reflectance spectra obtained for the $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ samples synthesized at 473 K. The strong optical absorption behavior was observed in all samples in the region of wavelength shorter than 500 nm, which corresponds to the blue region. As a result, the color of the samples is yellow, because blue is a complementary color to yellow. The position of the reflectance edge depends critically on the sample composition, and the maximum absorption between 450 and 500 nm was observed at the composition of $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ in comparison with the other samples.

The $L^*a^*b^*$ color coordinate data of the $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ pigments synthesized at 473 K are summarized in Table 1. The b^* value corresponding to yellow chromaticity depends on the La^{3+} content. The highest b^* value is obtained at $x = 0.10$, and, as a result, the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment gives the most yellowish hue, $b^* = +81.9$, which is higher than +80. The decrease of the b^* value in the $\text{Bi}_{0.85}\text{La}_{0.15}\text{VO}_4$ pigment is attributed to the formation of the impurity tetragonal BiVO_4 phase, which shows murky yellow hue.¹⁵

As mentioned above, the composition of the pigment was optimized to be $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$. In the following stage, the hydrothermal reaction temperature was optimized to further enhance the yellow hue of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment. For this purpose, the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigments were synthesized at 443

Table 1. $L^*a^*b^*$ color coordinate of the $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ pigments synthesized at 473 K

Sample	L^*	a^*	b^*
BiVO_4	89.0	-8.13	72.4
$\text{Bi}_{0.95}\text{La}_{0.05}\text{VO}_4$	85.9	-8.70	73.1
$\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$	86.8	-10.1	81.9
$\text{Bi}_{0.85}\text{La}_{0.15}\text{VO}_4$	87.8	-8.54	74.4

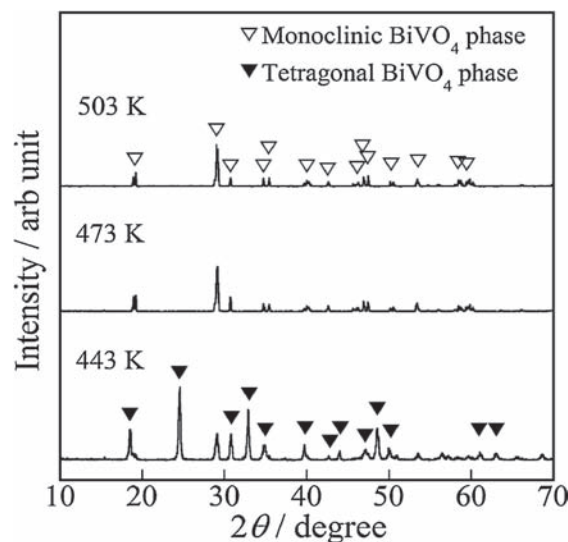


Figure 3. XRD patterns of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigments synthesized at 443, 473, and 503 K.

and 503 K. The XRD patterns of these samples are shown in Figure 3. A single phase of the monoclinic BiVO_4 structure was observed for the samples synthesized at 473 and 503 K. On the contrary, the tetragonal BiVO_4 phase was observed as a main component with a small amount of the monoclinic phase for the sample synthesized at 443 K. Accordingly, the hydrothermal reaction temperatures higher than 473 K are favorable to the formation of the monoclinic BiVO_4 phase in this system. Unfortunately, it is difficult to synthesize the sample above 503 K, because of the operating temperature limit of the Teflon® bottle.

Figure 4 illustrates the reflectance spectra of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ samples synthesized at 443, 473, and 503 K. For the samples obtained at 473 and 503 K, strong optical absorption behavior was observed in the blue region between 400 and 500 nm. In addition, the reflection of the yellow light (570–590 nm) of the samples was intensified by increasing the reaction temperature from 473 to 503 K. In particular, the reflection for the sample synthesized at 503 K is higher than that of the commercially available BiVO_4 . The reason for the difference in the reflection intensities for the samples synthesized at 473 and 503 K can be attributed to the difference of the crystallinity. In fact, the full width at half-maximum (FWHM) estimated from the XRD peak at around $2\theta = 29^\circ$ in Figure 3 was 0.2722 for the sample synthesized at 503 K, which was smaller than that for the sample synthesized at 473 K (0.2833). This result elucidates that the crystallinity of the former is higher than that of the latter. In the case of the sample synthesized at

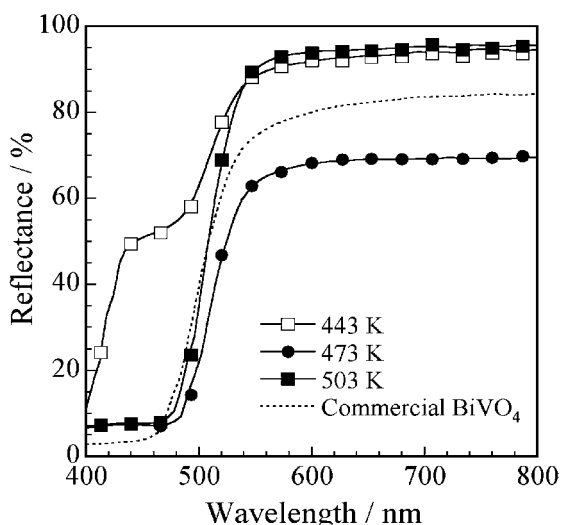


Figure 4. Reflectance spectra of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigments synthesized at 443, 473, 503 K, and commercial BiVO_4 .

Table 2. $L^*a^*b^*$ color coordinate of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigments synthesized at several temperatures

Hydrothermal temperature	L^*	a^*	b^*
443 K	95.1	-4.79	22.7
473 K	86.8	-10.1	81.9
503 K	92.8	-14.6	86.6
Commercially available BiVO_4	94.4	-16.7	76.9
Commercially available PbCrO_4	89.9	1.12	96.5

443 K, a two-step profile is observed and a significant decrease in the optical absorption is recognized in the blue light region, which is caused by the formation of the impurity tetragonal BiVO_4 phase.

The $L^*a^*b^*$ color coordinate data of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigments synthesized at 443, 473, and 503 K are also summarized in Table 2 with those of the commercially available BiVO_4 (BASF Sicopal® Yellow L1100) and PbCrO_4 (NIC NEO5GS) pigments. The highest b^* value (+86.6) was observed for the sample synthesized at 503 K, which exceeds the value of the commercially available BiVO_4 pigment, although it was not equal to that of the commercial PbCrO_4 pigment. The band gap energy of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment synthesized at 503 K was 2.45 eV, which is smaller than that of the commercially available BiVO_4 pigment (2.51 eV). This result can be ascribed to the enhancement of the hybridization of the Bi_{6s} and O_{2p} orbitals explained in the introduction.

However, in the case of the sample synthesized at 443 K, it becomes a little complicated to estimate the band gap energy by the simultaneous presence of monoclinic and tetragonal BiVO_4 phases. The main phase is the undesirable tetragonal one, and, as a result, the optical absorption due to the monoclinic phase becomes ineffective. The band gap energy of the tetragonal $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ phase was estimated to be 2.96 eV, because there is no formation of a hybrid orbital of Bi_{6s} and O_{2p} in the tetragonal BiVO_4 phase.¹⁶ Consequently, the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment synthesized at 443 K is murky yellow.

In summary, $\text{Bi}_{1-x}\text{La}_x\text{VO}_4$ pigments were successfully synthesized in a single phase by a hydrothermal reaction. The color of the pigments depends on the La^{3+} content and the hydrothermal reaction temperature. The most brilliant yellow hue was obtained for $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ synthesized at 503 K. The reason for the effective coloring of $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ is attributed to the lattice shrinkage to enhance the hybridization of Bi_{6s} and O_{2p} , which lowers the band gap energy. As a result, the yellow hue of the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment ($b^* = +86.6$) is higher by about 10 points than that of the commercially available BiVO_4 pigment ($b^* = +76.9$). Since BiVO_4 is an environment-friendly inorganic yellow pigment and La is also a nontoxic element, the $\text{Bi}_{0.90}\text{La}_{0.10}\text{VO}_4$ pigment should be an effective alternative to conventional toxic yellow pigments.

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