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Preparation of Novel Blue Turquoise-imitated Phosphate Pigments using Aluminum Hydroxide

Hiroaki Onoda and Ryota Sasaki

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H Onoda[1,*] and R Sasaki[1]
1 Kyoto Prefectural University, Kyoto, Japan
E-mail: h-onoda@kpu.ac.jp

Abstract. Recently, the use of harmful metals is restricted around world. However, because suitable substitutes have not been obtained, some materials containing harmful metals have been used in many fields. Therefore, novel inorganic pigments are required with suitable properties and without difficult production methods. As novel blue pigment, various copper aluminum phosphate hydroxides imitated with Turquoise, $CuAl_6(PO_4)_4(OH)_8$•$4H_2O$, were prepared by the mixing of copper nitrate solution, aluminum hydroxide solution, phosphoric acid, and sodium hydroxide solution. The obtained powders were estimated with X-ray diffraction (XRD), Infrared (IR) spectra, ultraviolet–visible (UV–Vis.) reflectance spectra, and L*a*b* color space. Furthermore, the other related compositions with Turquoise were also investigated. The color of phosphate pigment changed from light blue to green by heating at 500ºC. Samples prepared at pH 9 were easy to be green powder. Sample prepared at Cu/Al = 2/3 and then heated at 300ºC became dark green powder. The phosphate pigments from light blue to dark green were obtained in this preparation system.

1. Introduction

Recently, the use of harmful metals is restricted around world. However, because suitable substitutes have not been obtained, some materials containing harmful metals have been used in many fields [1,2]. For example, inorganic color pigments containing metals such as mercury, cadmium, and lead, have some merits, including high light stability, heat resistant coloring visibility, cost, etc [3-5]. In addition, because oxide pigments have low coloring and covering, they are difficult to use for paint and plastics [6]. Sulfate and nitrate pigments have lower heat resistance than oxide pigments, and require harmful and/or combustible gas to synthesize. Furthermore, it is difficult to obtain sulfide and nitrate pigments with repeatability [7,8]. Therefore, novel inorganic pigments are required with suitable properties and without difficult production methods.

There are some kinds of inorganic blue pigments, for example, that are available for use, Prussian blue, mixed metal oxide, cobalt blue, cerulean, cobalt chromium blue, and so on [9-12]. Some of these pigments also include harmful metals. Therefore, novel blue pigment without precious and harmful metals is required. We focus on the natural ore, Turquoise, $CuAl_6(PO_4)_4(OH)_8$•$4H_2O$, because this ore have no precious and harmful metals [13,14]. Natural ores have high light stability and heat resistance. Because of their solidity, they are expected to have applications for plastics, paint, ceramics, and so on.

We prepared the novel inorganic pigments imitated with Turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$, from cupper oxide, aluminum hydroxide, and phosphoric acid by heating [15]. The obtained materials had the XRD peaks of $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$ and CuO. However, the color of samples was dark, therefore, the different process is needed to obtain the novel blue inorganic pigments.

In this work, novel inorganic pigments imitated with Turquoise were synthesized by mixing of copper nitrate and aluminum hydroxide solution, phosphoric acid, and sodium hydroxide solution, and then heated to obtain their thermal products. The obtained materials were estimated from the viewpoint of pigment.

2. Experimental

Target material imitated of Turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$, was prepared in the following reaction.

$$Cu(NO_3)_2 + 6Al(OH)_3 + 4H_3PO_4 \rightarrow CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O + 2HNO_3 + 6H_2O \quad (1)$$

The total 0.5 mol/L of copper and aluminum solutions were prepared from copper nitrate and aluminum hydroxide in the ratio of Cu/Al=1/6. Then, the 0.5 mol/L of phosphoric acid (28 mL) was added to this copper and aluminum mixed solutions in Cu/Al/P=1/6/4. The mixed solutions were adjusted to pH 5, 7, and 9 with 8 mol/L of sodium hydroxide solution. The precipitates were filtered and dried. A part of precipitates were heated to 300, 500, 700ºC for 1 hour under air condition.

Other compositions, various Cu/Al ratio and Al/P ratio = 3/2, were also prepared using the same method. The chemical equations are as follows:

$$Cu(NO_3)_2 + 3Al(OH)_3 + 2H_3PO_4 \rightarrow CuAl_3(PO_4)_2(OH)_5 + 2HNO_3 + 4H_2O \quad (2)$$

$$3Cu(NO_3)_2 + 6Al(OH)_3 + 4H_3PO_4 \rightarrow Cu_3Al_6(PO_4)_4(OH)_{12} + 6HNO_3 + 6H_2O \quad (3)$$

$$2Cu(NO_3)_2 + 3Al(OH)_3 + 2H_3PO_4 \rightarrow Cu_2Al_3(PO_4)_2(OH)_7 + 4HNO_3 + 2H_2O \quad (4)$$

These mixed solutions in Cu/Al=1/3, 1/2 and 2/3 were adjusted with sodium hydroxide solution to pH 7. Their thermal products were prepared in the same process with Cu/Al=1/6. All chemicals were of commercial purity (Wako Chemical Industries Ltd., Osaka, Japan) and were used without further purification.

The chemical compositions of these materials were analyzed using X-ray diffraction (XRD) and Infrared (IR) spectra. The XRD patterns were recorded on an X-ray diffractometer (MiniFlex, Rigaku Corp., Akishima, Japan) using monochromatic CuKα radiation. IR spectra of samples were recorded on a HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method.

The color of phosphate pigments was estimated from the ultraviolet–visible (UV–Vis) reflectance spectra (UV2100; Shimadzu Corp., Kyoto, Japan) (reference compound: $BaSO_4$). The color of the pigments was also estimated with a TES135 plus color analyzer (TES Electrical Electronic Corp, Taipei, Taiwan). The L* value means the whiteness of powder, in which 100 is white, on the opposite site, 0 is black. The a* value means the redness of materials, with positive (maximum; +60) and negative (-60) values are corresponding with red and green, respectively. The b* value indicates the yellowish, in which positive (maximum; +60) and negative (-60) values are correspond with yellow and blue, respectively.

3. Results and discussion

3.1. Composition of $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$

Figure 1 shows XRD patterns of the samples heated at various temperatures. Sample without heating indicated the peaks of Turquoise, $Al(OH)_3$, and $Cu(OH)_2$. On the other hand, samples heated over 300ºC had some unknown peaks. Figure 2 shows IR spectra of the samples synthesized at various temperatures. Because samples had many absorption, it is difficult to assign their peaks. The peaks at about 1020 and 1385 cm^{-1} in IR spectrum of non-heated sample were due to the phosphate and nitrate anions.

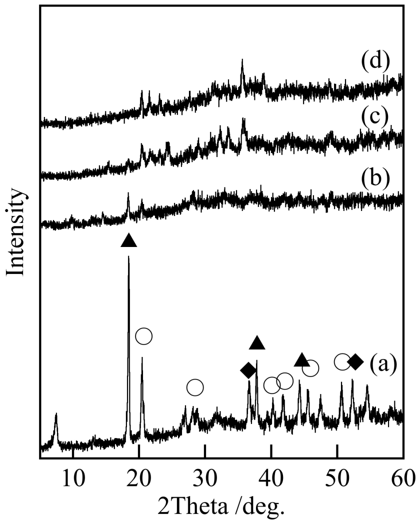

Fig. 1 XRD patterns of samples heated at various temperatures (pH 7), (a) R.T., (b) 300ºC, (c) 500ºC, (d) 700ºC, ○ ; $CuAl_6(PO_4)_4(OH)_8 \bullet 4H_2O$, ▲ ; $Al(OH)_3$, ◆ ; $Cu(OH)_2$.

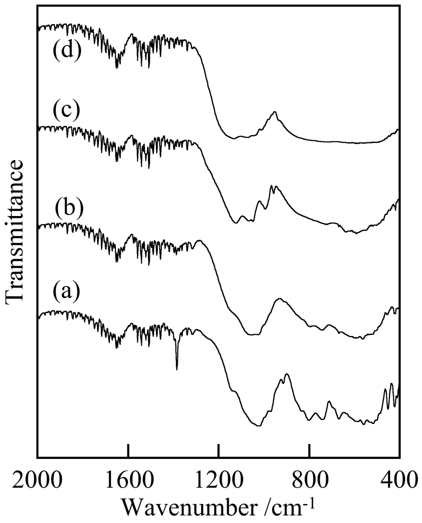

Fig. 2 IR spectra of samples heated at various temperatures (pH 7), (a) R.T., (b) 300ºC, (c) 500ºC, (d) 700ºC.

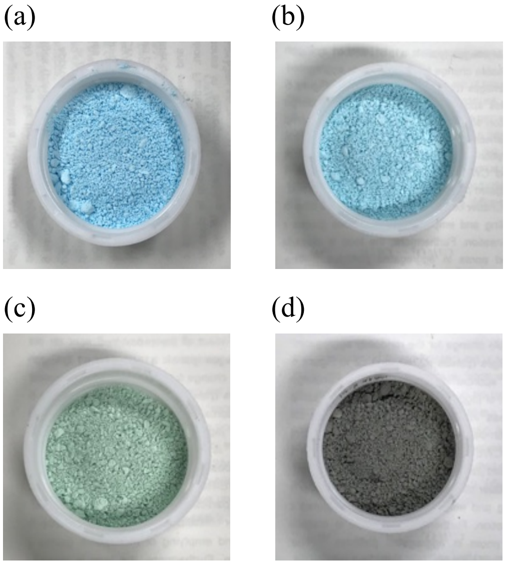

Fig. 3 Photographs of samples heated at various temperatures (pH 7), (a) R.T., (b) 300ºC, (c) 500ºC, (d) 700ºC.

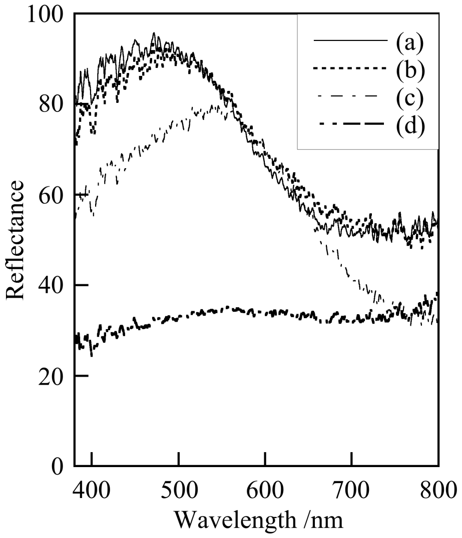

Fig. 4 Visible reflectance spectra of samples heated at various temperatures (pH 7), (a) R.T., (b) 300ºC, (c) 500ºC, (d) 700ºC.

Figure 3 shows photographs of the samples heated at various temperatures. Samples without heating and heated at 300ºC were light blue powders. By heating at 500ºC, the color of phosphate material changed to green. Sample heated at 700ºC turned dark color powder. Figure 4 shows the visible reflectance spectra of the samples prepared at various temperatures. The peak at 480 nm was observed in reflectance spectra of samples without heating and heated at 300ºC. This peak shifted to 560 nm by heating at 500ºC. Sample heated at 500ºC had weaker reflectance peak than those at lower temperatures. Sample heated at 700ºC had no peak at visible range. These change in the reflectance spectra were corresponding with those in photographs of samples.

Table 1 shows the L*a*b* values of the sample powders heated at various temperatures. The L* value became lower with the increasing of heating temperature, which is related with brightness. Sample heated at 700ºC had much L* value than others. Sample without heating indicated low a* value, due to green. The b* value changed from minus domain, blue, to plus domain, yellow, by heating at 500ºC. These results were corresponding with the color change of phosphate materials.

Table 2 shows the L*a*b* values of samples prepared at various pH values. The pH values produced small changes on L* and a* values. Sample prepared at pH 9 indicated +2 in b* value by heating at 300ºC. By heating at 700 and 500ºC, the b* value changed to the positive number in samples prepared at pH 5 and 7, respectively. Sample prepared at higher pH value was easy to indicate the positive b* value. The pH value had much influence on the b* value of phosphate pigment.

Table 1 L*a*b* values of samples heated at various temperatures (Cu/Al=1/6, pH 7)

Temp. /ºC	L*	a*	b*
R.T.	82.71	-11.92	-8.52
300	79.52	-9.02	-6.03
500	77.75	-9.44	2.62
700	56.19	-1.21	4.75

Table 2 L*a*b* values of samples prepared at various pH values (Cu/Al=1/6, 300ºC)

pH	L*	a*	b*
5	81.13	-10.54	-5.96
7	79.52	-9.02	-6.03
9	73.93	-6.84	2.05

3.2. Other compositions

To obtain a novel blue pigment, the related compositions with $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$ were also estimated. Because we prepared the materials at Cu/Al = 1/3, 1/2, and 2/3 in previous paper [15], the compositions with the same Cu/Al ratios were studied. Figure 5 shows the photographs of the samples prepared at various Cu/Al ratios. Samples prepared at Cu/Al = 1/6 and 1/3 were light blue powders. The blue tone became weak in sample prepared at Cu/Al = 1/2. Further, sample prepared at Cu/Al = 2/3 was green powder. Table 3 shows the L*a*b* values of the samples prepared at various Cu/Al ratios. The L* value became smaller with the increasing of Cu/Al ratio. Sample prepared at Cu/Al =2/3 had the much different a* and b* values from others.

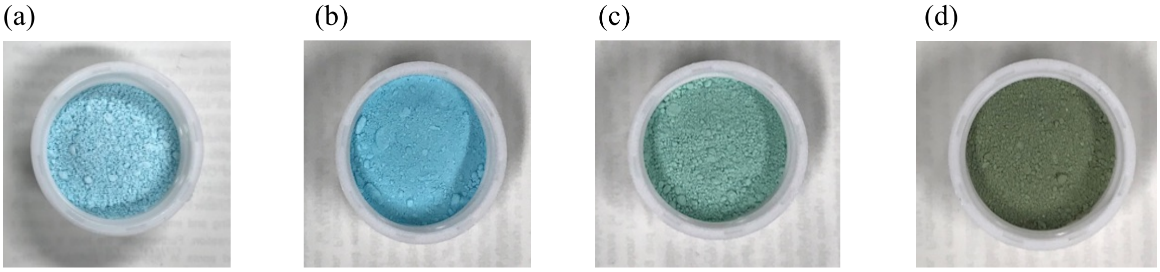

Fig. 5 Photographs of samples prepared in various Cu/Al ratios (300ºC), (a) 1/6, (b) 1/3, (c) 1/2, (d) 2/3.

Table 3 L*a*b* values of samples prepared at various Cu/Al ratios (pH 7, 300ºC)

Cu/Al	L*	a*	b*
1/6	81.13	-10.54	-5.96
1/3	74.21	-17.53	-9.66
1/2	76.02	-14.78	-0.11
2/3	59.96	-6.90	10.87

4. Conclusions

Novel phosphate pigments imitated with Turquoise were prepared by the mixing of copper nitrate solution, aluminum hydroxide solution, phosphoric acid, and sodium hydroxide solution. The color of phosphate pigment changed from light blue to green by heating at 500ºC. Samples prepared at pH 9 were easy to be green powder. Sample prepared at Cu/Al=2/3 and then heated at 300ºC became dark green powder. The phosphate pigments from light blue to dark green were obtained in this preparation system.

5. References

[1] Amat A, Millani C, and Fantacci S 2016 *RSC Adv.* **6** 36336.
[2] Tao Z, Zhang W, Huang Y, Wei D, and Seo H J 2014 *Solid State Sci.* **34** 78.
[3] Radepont M, Conquinot Y, Janssens K, Ezrati J J, and Cotte M 2015 *J. Anal. At. Spectrom.* **30** 599.
[4] Rosi F, Grazia C, Gabrieli F, Romani A, Paolantoni M, Vivani R, Brunetti B G, Colomban P, and Miliani C 2016 *Microchem. J.* **124** 856.
[5] Li M, Wand J, and Ma Q 2015 *J. Cultural Heritage* **16(4)** 575.
[6] Jiang S, Peng L, Guo R, Miao D, Shang S, Xu J, and Li A 2016 *Ceram. Intern.* **42(16)** 19386.
[7] C. Migurei C, Pinto J V, Clarke M, and Melo M J 2014 *Dyes Pig.* **102** 210.
[8] Ohashi M, Kusumoto K, Sugiyama T, and Kato K 2016 *J. Ceram. Soc. Jpn.* **124(9)** 959.
[9] Ali I O, Salam T M, Thabet M S, El-Nasser K S, and Hassan A M 2013 *Mater. Chem. Phys.* **140** 81.
[10] Gaudon M, Robertson L C, Lataste E, Duttine M, Ménétrier M, and Demourgues A 2014 *Ceram. Intern.* **40** 5201.
[11] Angelin E M, Bacci M, Bartolozzi G, Cantisani E, and Picollo M 2017 *Spectrochim. Acta* **173** 510.
[12] Jose S and Reddy M L 2013 *Dyes Pigments* **98** 540.

[13] Cejka J, Sejkora J, Macek I, Malíková R, Wang L, Scholz R, Xi Y and Frost R L, 2015 *Spectrochim. Acta* **149** 173.
[14] Othmane G, Hull S, Fayek M, Rouxel O, Geagea M L and Kyser T K 2015 *Chem. Geol.* **395** 41.
[15] Onoda H and Sasaki R, 2019 *Mater. Res. Innov.*, **23(5)** 266.