

Preparation of Novel Scorzalite Imitated Phosphate Pigments

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Abstract: Novel phosphate pigments imitated with Scorzalite, $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$, were prepared from iron and aluminum nitrate solutions, ascorbic acid, and phosphoric acid with pH adjustments (pH 5, 7, 9). The obtained precipitates were heated at 300, 500, and 700 °C for 1 h. The precipitates and their thermal products were estimated with X-ray diffraction (XRD), Infrared (IR) spectra, ultraviolet-visible (UV-Vis) reflectance spectra, and $L^*a^*b^*$ color space. The precipitated sample was not clearly colored, but it turned orange to red when heated. Samples prepared at low pH showed higher whiteness than samples prepared at high pH. The theoretical amount of ascorbic acid was sufficient to completely reduce iron during the adjustment. This study showed the possibility of novel inorganic phosphate red pigment.

Key words: Iron aluminum phosphate, natural ore, red pigment.

1. Introduction

The use of toxic metals is restricted around the world, and recently the limits have become increasingly strict. However, due to the difficult production of appropriate alternatives, some of the material including the harmful metal is used in many fields [1, 2]. For example, inorganic colored pigments containing toxic metals such as mercury, cadmium, and lead have several benefits such as high light stability, heat-resistant coloring visibility, and cost [3-5]. In addition, oxide pigments are difficult to use in paints and plastics due to their low coloring and covering power [6]. Sulfate and nitride pigments have the disadvantage of lower heat resistance than oxide pigments, and their synthesis requires harmful and flammable gases. In addition, it is difficult to obtain sulfide and nitride pigments with high reproducibility [7, 8]. Therefore, there is a need for new inorganic pigments with appropriate properties and without difficult manufacturing methods.

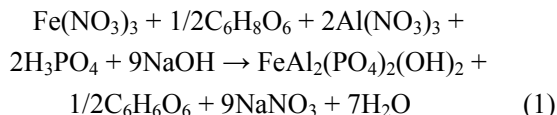
Natural ore has high light stability and heat resistance. Due to their low solubility, they are expected to be applied to various fields such as plastics, paints and ceramics. Because turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ does not contain precious and harmful metals [9, 10], we prepared novel inorganic pigments that imitate this ore by dry and wet processes [11, 12]. The resulting material had the X-ray diffraction (XRD) peaks of $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ and CuO. However, the color of the sample synthesized by the dry method was dark, while the material prepared by the wet method was light blue.

In this work, we focus on other natural ore, Scorzalite, $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$. Scorzalite is generally a dark blue ore, but can be green, purple or orange depending on where it is mined. The novel inorganic pigments imitated with Scorzalite were prepared from iron and aluminum nitrate solutions, ascorbic acid, phosphoric acid, and sodium hydroxide solution, and then heated to obtain various color pigments. The obtained materials were estimated from the viewpoint of pigment.

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2. Experimental Procedure

Target material with the chemical composition of Scorzalite, $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$, was prepared in following reactions.



The total 0.5 mol/L of iron and aluminum solutions were prepared from iron nitrate and aluminum nitrate, and iron nitrate and aluminum nitrate in the ratio of $\text{Fe}/\text{Al} = 1/2$. Ascorbic acid was added to reduce iron cation from +III to +II in the ratio of $\text{Asc}/\text{Fe} = 1/2$, 1.25/2, 1.5/2. The ratio of $\text{Asc}/\text{Fe} = 1/2$ is equivalent, but in order to completely reduce iron, the conditions added in excess were also examined. Then, the 0.5 mol/L of phosphoric acid (28 mL) was added to this iron and aluminum mixed solutions in $\text{Fe}/\text{Al}/\text{P} = 1/2/2$. 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, 700 °C for 1 h under air condition. 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 XRD and Infrared (IR) spectra. The XRD patterns were recorded on an X-ray diffractometer (MiniFlex, Rigaku Corp., Akishima, Japan) using monochromatic $\text{CuK}\alpha$ 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; +128) and negative (-128) values corresponding with red and green, respectively [13]. The b^* value indicates the yellowness, in which positive (maximum; +128) and negative (-128) values are corresponding with yellow and blue, respectively.

3. Experimental Results

3.1 Influence of Heating Temperature

Fig. 1 shows XRD patterns of the samples heated at various temperatures. Samples without heating and heated at 300 °C and 500 °C were amorphous state. On the other hand, sample heated at 700 °C had weak unknown peaks. In general, a sample prepared using an aqueous solution tends to be amorphous. This trend was also confirmed in this study. The similar results were obtained for samples prepared at pH 5 and 9 (not shown).

Fig. 2 shows IR spectra of the samples heated at various temperatures. The precipitated samples had peaks at 1,070, 1,380, and 1,640 cm^{-1} , which corresponded to phosphate ions, nitrate ions, and water, respectively. The peaks due to nitrate ions and water disappeared by heating at 300 °C. It was confirmed that the sample prepared in this study was a phosphate-based material.

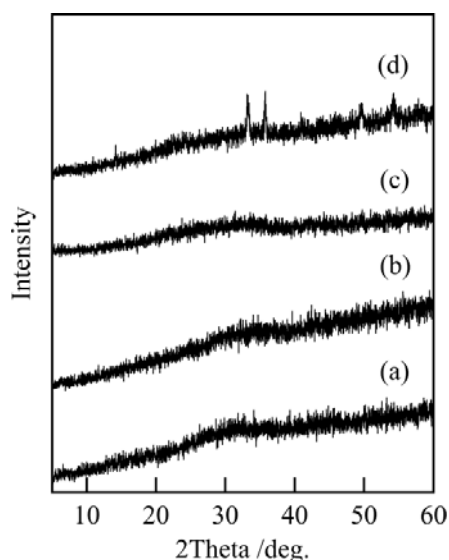


Fig. 1 XRD patterns of samples heated at various temperatures (pH 7, $\text{Asc}/\text{Fe} = 1.25/2$), (a) R.T. (room temperature), (b) 300 °C, (c) 500 °C, (d) 700 °C.

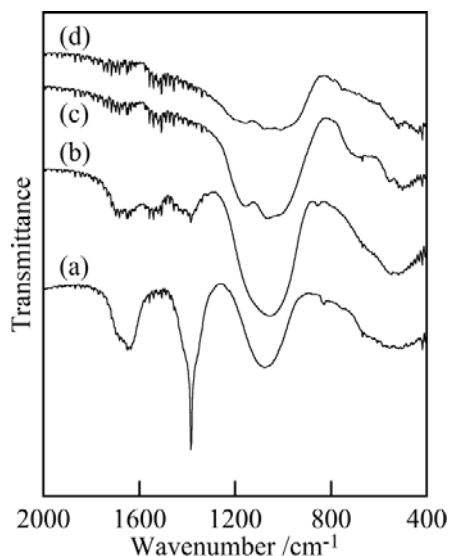


Fig. 2 IR spectra of samples heated at various temperatures (pH 7, Asc/Fe = 1.25/2), (a) R.T. (room temperature), (b) 300 °C, (c) 500 °C, (d) 700 °C.

Fig. 3 shows photographs of the samples heated at various temperatures. The precipitated sample did not show a clear color. As mentioned above, Scorzalite can take a variety of colors, including deep blue, green, purple and orange, but samples that actually imitated its composition did not show any color. The reason is related to the action of ascorbic acid. Since iron in the composition of this natural ore is in a divalent state, ascorbic acid was used as a reducing agent during sample preparation. If a trivalent iron compound is precipitated, it becomes a strong brown color. Therefore, when trivalent iron remains even a little, the color of the sample is strongly affected. Further, if the iron is completely divalent, a green powder should be obtained [14]. In this study, powders that were neither green nor brown were obtained. Ascorbic acid reduced most of the iron, but trace amounts of iron were thought to be trivalent. By heating at 300 °C, the sample powder

turned orange. When heated to a higher temperature, the redness of the sample increased. This is probably because the iron in the sample became trivalent.

Fig. 4 shows the UV-Vis reflectance spectra of the samples heated at various temperatures. By heating to 300 °C, the reflectance increased at longer wavelengths than 600 nm. This corresponds to the sample becoming reddish. Further, it is shown that by heating to a high temperature, the overall reflectance is lowered and the sample is darkened. This change in reflectance corresponds to the color change shown in Fig. 3.

Table 1 shows the $L^*a^*b^*$ values of the sample powders heated at various temperatures. As the heating temperature increased, the L^* value decreased. On the other hand, the a^* value was improved by heating. Samples heated to 300 °C and 500 °C showed high b^* values. These results clearly showed that the sample heated at 700 °C was the most red.

3.2 Influence of pH and Ascorbic Acid

To obtain various phosphate pigments, samples were prepared by changing the pH values and the ratio of ascorbic acid. Fig. 5 shows UV-Vis reflectance spectra of the samples prepared at various pH values. Samples prepared at low pH showed higher reflectance, however the change of waveform was not observed. This indicates that sample prepared at a low pH is a whitish powder.

Table 2 shows the $L^*a^*b^*$ values of the samples prepared at various conditions. Samples prepared at high pH showed low L^* values. The a^* and b^* values had small changes due to different pH during adjustment. In this study, excess ascorbic acid was added to reduce all the added iron, but the change in

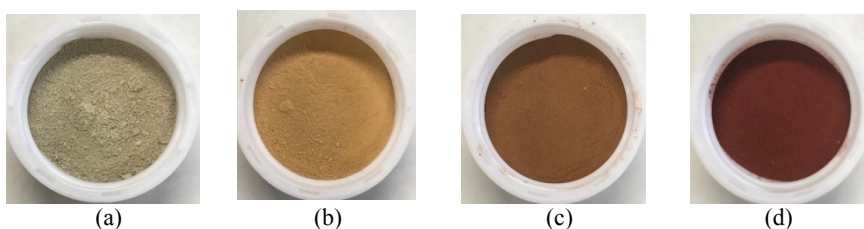


Fig. 3 Photographs of samples heated at various temperatures (pH 7, Asc/Fe = 1.25/2), (a) R.T. (room temperature), (b) 300 °C, (c) 500 °C, (d) 700 °C.

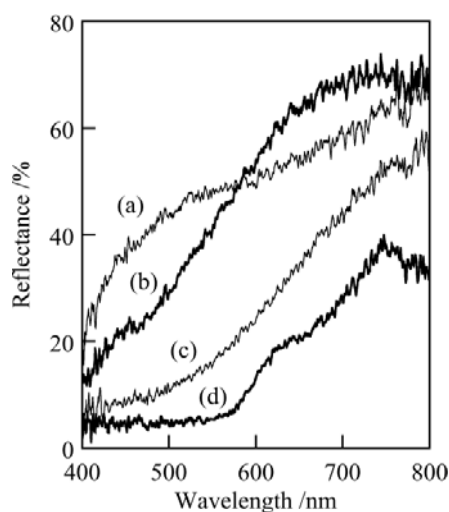


Fig. 4 UV-Vis reflectance spectra of samples heated at various temperatures (pH 7, Asc/Fe = 1.25/2), (a) R.T. (room temperature), (b) 300 °C, (c) 500 °C, (d) 700 °C.

Table 1 $L^*a^*b^*$ values of samples heated at various temperatures (pH 7, Asc/Fe = 1.25/2).

Temp./°C	L^*	a^*	b^*
R.T.	71.14	1.17	12.21
300	65.78	11.48	27.25
500	48.29	17.32	22.97
700	33.02	29.19	16.43

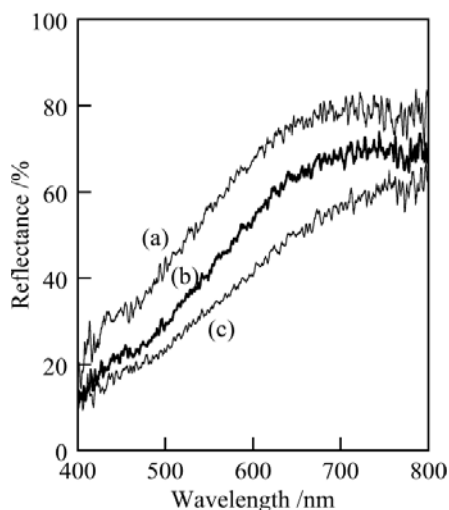


Fig. 5 UV-Vis reflectance spectra of samples prepared at various pH values and then heated at 300 °C (Asc/Fe = 1.25/2), (a) 5, (b) 7, (c) 9.

$L^*a^*b^*$ values with the amount of ascorbic acid was small. This meant that it was fully reduced by the theoretical amount of ascorbic acid and that it did not change when added further.

Table 2 $L^*a^*b^*$ values of samples prepared at various conditions (300 °C).

pH	Asc/Fe	L^*	a^*	b^*
5	1.25/2	75.53	8.28	25.93
7	1.25/2	65.78	11.48	27.25
9	1.25/2	61.06	11.39	25.27
7	1/2	73.41	11.52	27.49
7	1.5/2	72.45	10.90	25.69

4. Conclusions

Novel phosphate pigments imitated with Scorzalite were prepared from iron and aluminum nitrate solution, ascorbic acid, phosphoric acid, and sodium hydroxide solution. The precipitated sample did not have a clear color, but when heated, it showed an orange to red color. Samples prepared at low pH were whiter powder than samples prepared at high pH. The theoretical amount of ascorbic acid was sufficient for the reduction of iron during the adjustment, and no excess was required. A novel inorganic phosphate red pigment was obtained by this study.

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