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Synthesis of Novel Phosphate Pigments Based on Manganese Lazulite

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Abstract: Novel inorganic pigments based on manganese lazulite compositions were obtained by aqueous solution precipitation and subsequent heating. The obtained samples were evaluated by XRD (X-ray diffraction), infrared spectroscopy, UV-visible reflectance spectra, and L*a*b* values. In addition, changes after exposure to acid and base solutions and the coloring power compared to titanium dioxide or zinc oxide were evaluated. In the XRD patterns of the samples, XRD peaks due to lazulite were observed, although they were in a mixed state. The samples were generally light red, becoming orange at 500 °C and purple at 700 °C. The samples were sensitive to acid and base solutions, which darkened the color of the samples. The coloring power of the samples in this study was close to that of zinc oxide.

Key words: Lazulite, natural ore, phosphate pigments, coloring power.

1. Introduction

Today, the development of science and technology has led to the use of a very large number of compounds, among which the use of toxic heavy metals has been suppressed worldwide [1, 2]. However, many of them are unavoidably used due to the lack of alternative materials with appropriate physical properties. In the field of inorganic pigments, those containing clearly toxic metals, such as cadmium red and cinnabar, are still in use [3, 4]. Therefore, inorganic pigments that do not contain toxic heavy metals are required to replace them.

Several oxides, sulfides, and nitrides are known as inorganic pigments [5-7]. However, compared to organic pigments, there are fewer types, and pigments with a wider variety of colors are required. Furthermore, sulfides and nitrides have problems with heat resistance, which is one of the strengths of inorganic pigments [8, 9]. In addition to color, inorganic pigments are also required to have resistance to acids and bases [10, 11].

Natural materials such as green earth and yellow earth are also utilized in inorganic pigments [12, 13]. Natural compositions are expected to be chemically stable because they have existed under conditions of exposure to the weather for many years. Therefore, inorganic pigments have been prepared with reference to the composition of natural ores [14]. Lazulite is a phosphate ore with a composition represented by $MgAl_2(PO_4)_2(OH)_2$ [15]. This Mg site can be replaced by Fe. Turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$, is a very well-known ore containing phosphate and aluminum ions [16]. Based on these compositions, copper lazulite with the Mg site replaced by Cu was evaluated as well [17]. By further developing materials with various Cu/Fe ratios, blue-yellow-orange pigments were obtained [18]. In this study, novel inorganic pigments based on the composition of manganese lazulite were

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prepared and their physical properties were evaluated in order to further increase the diversity of pigments with this lazulite composition.

2. Experimental

A 0.5 mol/L manganese nitrate solution was prepared by dissolving manganese powder in nitric acid. This solution was mixed with 0.5 mol/L aluminum nitrate solution in the ratio of Mn/Al=1/2. The mixed solution was blended with 2.0 mol/L phosphoric acid with Mn/Al/P = 1/2/2. The precipitate was further formed by adjusting the aqueous solution to pH 5 with 8 mol/L sodium hydroxide solution, filtered, and dried. A portion of the sample was heated at 200, 250, 300, 500, and 700 °C for 1 h. Samples with Mn/Al/P=1/4/2, 1/1/1, and 2/1/2 were also prepared by the same method. These ratios correspond to the compositions of $Mn_{1/2}Al_2(PO_4)_2(OH)$, $MnAl(PO_4)(OH)_2$, and $Mn_2Al(PO_4)_2(OH)$.

The crystal structures and covalent bonds of these materials were analyzed using XRD (X-ray diffraction) patterns and IR (infrared) spectra, respectively. XRD patterns were recorded on an X-ray diffractometer (MiniFlex, Rigaku Corporation, Akishima, Japan) using monochromatic CuKα radiation (30 kV, 15 mA, 3 °/min, step size: 0.02°). IR spectra of the samples were recorded by KBr disk method (Resolution: 4 cm^{-1}, 16 times scanned) using a HORIBA FT-IR 720 (HORIBA Corporation, Kyoto, Japan).

The color of phosphate pigments was estimated from the UV-Vis (ultraviolet-visible) reflectance spectrum (UV2100; Shimadzu Corporation, Kyoto, Japan) (reference compound: $BaSO_4$). The color of the materials was evaluated using a TES135 plus color analyzer (TES Electrical Electronic Corp, Taipei, Taiwan). The L* value represents the whiteness of the powder, with 100 corresponding to white and the opposite 0 to black; the a* value represents the redness of the material, with positive and negative values corresponding to red and green, respectively; the b* value represents the yellowness, with positive and negative values corresponding to yellow and blue, respectively.

The sample (0.1 g) was exposed to 0.1 wt% sulfuric acid solution (100 mL) or 0.1 wt% sodium hydroxide solution (100 mL) for 24 h, and then filtered to obtain the residue. The acid and base resistances of the samples were evaluated from the colors and yields of the residues. The color change ΔE before and after the acid and base resistance evaluation was calculated from the following formula.

$$\Delta E^* = [(L^*_{after} - L^*_{before})^2 + (a^*_{after} - a^*_{before})^2 + (b^*_{after} - b^*_{before})^2]^{1/2} \quad (1)$$

The coloring power was evaluated by mixing with TiO_2 or ZnO, commonly used white pigments: 0.1 g sample was mixed with 0.1 g TiO_2 or ZnO and then the L*a*b* values of the mixture were measured. The color difference $\Delta E_{original}$ between the white pigment and the sample was calculated using the following formula.

$$\Delta E_{original} = [(L^*_{white} - L^*_{sample})^2 + (a^*_{white} - a^*_{sample})^2 + (b^*_{white} - b^*_{sample})^2]^{1/2} \quad (2)$$

In a similar manner, $\Delta E_{mixture}$ was calculated from the L*a*b* values of the white pigments and mixtures.

$$\Delta E_{mixture} = [(L^*_{white} - L^*_{mixture})^2 + (a^*_{white} - a^*_{mixture})^2 + (b^*_{white} - b^*_{mixture})^2]^{1/2} \quad (3)$$

Contrast values were calculated using these values.

$$\text{Contrast value} = (\Delta E_{mixture} / \Delta E_{original}) \times 100 \quad (4)$$

A contrast value of 50% indicates that the white pigment and the sample have equal coloring power.

3. Experimental Results

3.1 Composition and Color of Samples Prepared in Mn/Al=1/2

Fig. 1 shows XRD patterns of samples prepared with Mn/Al=1/2 and then heated at various temperatures. A peak was observed only around 30° for samples heated below 300 °C. The composition of the sample could not be determined because of the low number of peaks. The sample heated at 500 °C showed peaks due to aluminum phosphate, while the sample heated at 700 °C showed a variety of peaks due to aluminum phosphate, lazulite, and manganese phosphate, with unidentifiable peak [19-21]. These results indicate that heating to 700 °C is

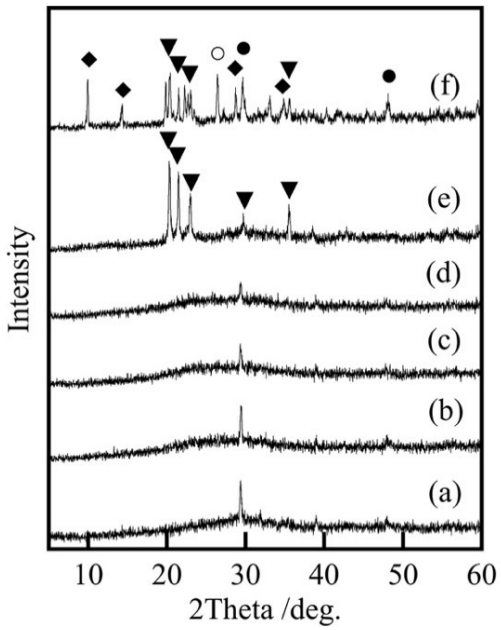

Fig. 1 XRD patterns of samples heated at various temperatures (Mn/Al=1/2), (a) R.T., (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 500 °C, (f) 700 °C, ●: Lazulite, ◆: $Mn_3(PO_4)_2$, ▼: $AlPO_4$, ■: Mn_2O_3, ○: unknown.

necessary for crystallization of the lazulite composition and that further investigation of conditions is necessary to obtain only the lazulite structure.

Fig. 2 shows the IR spectra of samples prepared with Mn/Al=1/2 and then heated at various temperatures. Samples heated below 300 °C have a relatively strong peak at 1,380 cm^{-1}, which is due to nitrate ions. Heating to higher temperatures volatilizes the nitrate ions, resulting in the disappearance of this peak in samples heated to higher temperatures. The broad peak at 1,650 cm^{-1} is due to crystalline water or adsorbed water, which also disappeared after heating to high temperature. The broad peak at 1,100 cm^{-1} in the spectra of all samples is due to phosphate ions [22]. The sample heated at 700 °C had some small peaks, indicating the formation of specific compounds. These results corresponded to the XRD results.

Fig. 3 shows photographs of samples prepared with Mn/Al = 1/2 and then heated at various temperatures. Samples heated at 200 to 300 °C were reddish powders, turning yellow at 500 °C and violet at 700 °C. Fig. 4 shows the visible light reflectance spectra of samples heated at various temperatures. Samples without heating exhibited high reflectance, while the reflectance of the heated samples decreased as the temperature increased. The unheated sample and the sample heated at 200 °C had lower reflectance around 500 nm than the reflectance at other wavelengths, corresponding to redness; the sample heated at 700 °C had higher reflectance around 400 and 800 nm than the reflectance at other wavelengths, corresponding to violet.

Table 1 shows the L*a*b*, C*, and h^o values for samples prepared with Mn/Al=1/2 and subsequently heated at various temperatures. The chroma C* and hue angle h^o are given by the following equations.

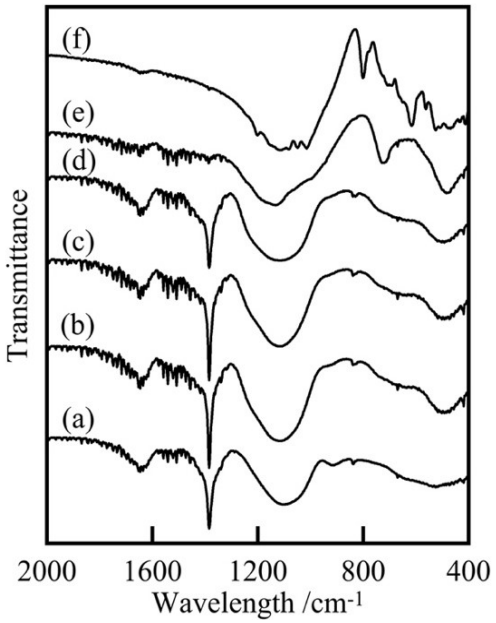

Fig. 2 IR spectra of samples heated at various temperatures (Mn/Al=1/2), (a) R.T., (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 500 °C, (f) 700 °C.

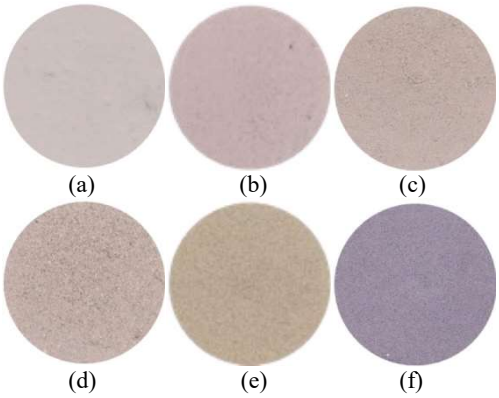

Fig. 3 Photographs of samples heated at various temperatures (Mn/Al=1/2), (a) R.T., (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 500 °C, (f) 700 °C.

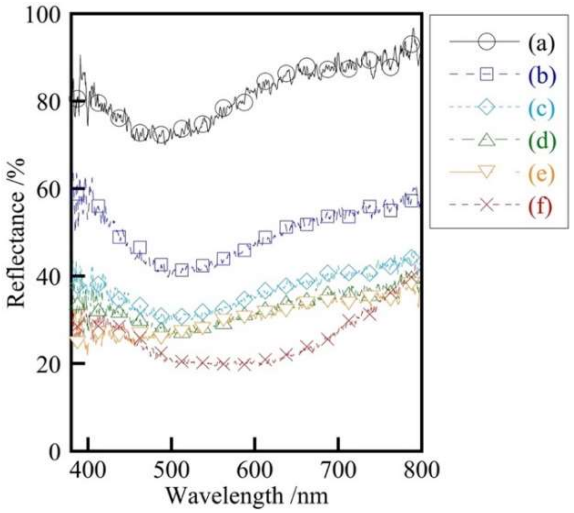

Fig. 4 UV-Vis. reflectance spectra of samples heated at various temperatures (Mn/Al=1/2), (a) R.T., (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 500 °C, (f) 700 °C.

$$C^* = \{(a^*)^2 + (b^*)^2\}^{1/2} \quad (5)$$

$$h^o = \tan^{-1}(b^*/a^*) \quad (6)$$

As the heating temperature increased, the L* values of the samples decreased. Samples heated at 200 °C to 300 °C showed higher a* values compared to the other samples resulting in a reddish tint. The b* values were high for the sample heated at 500 °C and low for the sample heated at 700 °C. The C* values were in a narrow range from 5.1 to 7.4, and all samples exhibited low chroma. From the h^o values, the unheated samples were orange, those heated at 200 to 300 °C were red, those heated at 500 °C were yellow, and those heated at 700 °C were violet.

3.2 Acid/Base Resistance and Coloring Power of Samples Prepared in Mn/Al=1/2

Table 2 shows the recovery ratio and L*a*b* values after the samples were immersed in acid or base solution. The ΔE^* values are also shown, comparing the hue of the color with that before immersion. The recovery ratios for both acids and bases were low, less than 50% for most of the samples. This is related to the tendency of aluminum and phosphate ions to form easily soluble compounds. The hue change ΔE^* had many values around 10, indicating that the color of the samples changed as they were immersed. The effect of different heating temperatures on these was small.

Table 3 shows the results of the coloring power of the samples. The coloring power of the samples ranged from 40%-27% for titanium dioxide and 47%-39% for zinc oxide. The samples prepared in this study were found to have slightly lower coloring power than zinc oxide. Based on the fact that titanium dioxide and zinc oxide have excellent coloring power and are widely used as white pigments, slightly lower coloring power than these was considered to have sufficient potential for active use.

Table 1 L*a*b*, C*, h^o values of samples heated at various temperatures (Mn/Al=1/2).

Temp. (℃)	L*	a*	b*	C*	h°
R.T.	90.02	3.98	3.23	5.1	39.0
200	70.46	5.87	-0.08	5.9	359.2
250	63.25	6.14	1.40	6.3	12.8
300	60.58	4.99	1.76	5.3	19.4
500	59.80	3.85	6.37	7.4	58.8
700	51.75	3.38	-6.33	7.2	298.1

Table 2 Residual ratio and color difference of samples exposed to H_2SO_4 or NaOH solution (%).

Acid/base	Temp. (℃)	Yield (%)	L*	a*	b*	ΔE^*
H_2SO_4	R.T.	3.8	87.95	8.32	7.09	6.2
H_2SO_4	200	23.0	62.10	7.23	5.24	10.0
H_2SO_4	250	19.7	54.97	9.24	7.24	10.6
H_2SO_4	300	40.5	50.64	5.25	8.39	12.0
H_2SO_4	500	35.6	48.01	5.13	7.11	11.9
H_2SO_4	700	50.9	62.57	3.12	2.21	13.8

Table 2 to be continued

NaOH	R.T.	40.8	76.01	3.66	8.44	15.0
NaOH	200	52.9	65.69	4.72	5.21	7.2
NaOH	250	31.2	58.06	4.94	5.07	6.5
NaOH	300	47.8	50.92	4.38	5.92	10.5
NaOH	500	30.9	49.06	10.30	3.31	12.9
NaOH	700	32.1	51.03	3.31	-1.04	5.3

Table 3 ΔE^* and contrast values of samples prepared at various temperatures (Mn/Al = 1/2).

	Temp. (°C)	$\Delta E_{original}$*	ΔE_{mix}*	Contrast (%)
TiO_2	R.T.	10.8	4.3	40
TiO_2	200	29.8	10.0	33
TiO_2	250	37.0	12.7	34
TiO_2	300	39.5	15.0	38
TiO_2	500	40.5	14.6	36
TiO_2	700	48.6	13.1	27
ZnO	R.T.	10.9	4.9	45
ZnO	200	29.9	13.0	44
ZnO	250	37.0	16.5	45
ZnO	300	39.5	17.6	45
ZnO	500	40.5	19.1	47
ZnO	700	48.6	19.0	39

3.3 Samples Prepared in Various Mn/Al Ratios

Fig. 5 shows XRD patterns of samples prepared at various Mn/Al ratios and subsequently heated at 700 °C. Samples with Mn/Al = 2/1 and 1/1 showed only aluminum phosphate peaks. Despite the relatively low ratio of Al in these samples, crystallization of aluminum phosphate occurred, but the reason for this could not be identified. Samples prepared with Mn/Al=1/2 and 1/4 showed the peaks of $AlPO_4$, lazulite, and $Mn_3(PO_4)_2$ [19-21]. The manganese phosphate peaks were observed in the sample with lower manganese content, and this factor is also unknown.

Table 4 shows the hue results for samples prepared at various Mn/Al ratios and subsequently heated at 300 or 700 °C. The L* values decreased as the ratio of Al increased. In general, aluminum tends to form white compounds, and the present results were the opposite of that. All a* values were positive, indicating that all samples had a reddish tint; b* values were positive in all except one sample, indicating that many samples had a yellowish tint. All samples had C* values lower than 11 indicating low chroma, and the hue angle of the samples varied from 298° to 83°. Furthermore, most of these samples showed less than 50% recovery when immersed in acid or base, indicating that they are sensitive to acid and base regardless of Mn/Al composition (not shown).

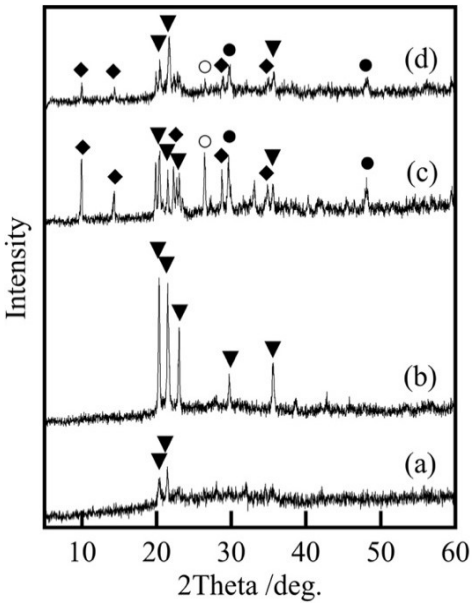

Fig. 5 XRD patterns of samples prepared in various Mn/Al ratios and then heated at 700 °C, (a) 2/1, (b) 1/1, (c) 1/2, (d) 1/4, ●: Lazulite, ◆: $Mn_3(PO_4)_2$, ▼: $AlPO_4$, ■: Mn_2O_3, ○: unknown.

Table 4 L*a*b*, C*, hº values of samples prepared in various Mn/Al ratios, and then heated at 300 °C or 700 °C.

Temp. (°C)	Mn/Al	L*	a*	b*	C*	h°
300	2/1	82.20	2.75	2.72	3.9	44.7
300	1/1	67.70	5.97	4.77	7.6	38.7
300	1/2	60.58	4.99	1.76	5.3	19.4
300	1/4	58.39	2.74	10.03	10.4	74.7
700	2/1	81.59	0.42	3.58	3.6	83.4
700	1/1	82.99	4.70	9.48	10.6	63.6
700	1/2	51.75	3.38	-6.33	7.2	298.1
700	1/4	67.10	3.82	0.19	3.8	2.8

4. Conclusions

Novel inorganic phosphate pigments were prepared by precipitation in aqueous solution and subsequent heating, using the composition of the natural mineral lazulite as a reference. The obtained samples were evaluated from their chemical composition, hue, acid and base resistance, and coloring power. The formation of compounds of lazulite composition was suggested by heating to 700 °C, although they were not pure but a mixture. The samples were generally reddish, but the chroma of the samples was not high. The samples prepared in this study were sensitive to acids and bases. The coloring power was evaluated by mixing with titanium dioxide or zinc oxide, and was found to have a coloring power similar to that of commonly used zinc oxide. Samples were prepared by varying the Mn/Al ratio, suggesting the formation of a lazulite structure even at Mn/Al=1/4.

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