Synthesis of novel red phosphate pigments from manganese carbonate to imitate natrophilite

(Síntese de novos pigmentos de fosfato vermelho de carbonato de manganês como imitação da natrofilita)

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Abstract

A novel red pigment, sodium manganese phosphate ($NaMnPO_4$), imitating natrophilite, was synthesized from manganese carbonate by heating under various conditions. The powders obtained were investigated by X-ray diffraction (XRD) analysis, infrared spectroscopy, ultraviolet-visible reflectance spectroscopy, and L*a*b* color space. Samples synthesized at 500-800 °C presented XRD patterns associated with $NaMnPO_4$. By heating at a higher temperature, the samples exhibited lighter color. The sample synthesized at 700 °C indicated the highest a* value. Furthermore, the effects of varying relative amounts of constituents were also studied. The temperature and period of heating, volume of water, and phosphate content affected the color phase of the pigments.

Keywords: red pigment, natural ores, phosphate materials.

Resumo

*Um novo pigmento vermelho, fosfato de sódio e manganês ($NaMnPO_4$), imitando a natrofilita, foi sintetizado a partir de carbonato de manganês por aquecimento em várias condições. Os pós obtidos foram investigados por análise de difração de raios X, espectroscopia no infravermelho, espectroscopia de reflectância ultravioleta-visível e espaço de cor L*a *b*. Amostras sintetizadas a 500-800 °C apresentaram difratogramas de raios X associados ao $NaMnPO_4$. Ao aquecer em temperatura mais elevada, as amostras exibiram cor mais clara. A amostra sintetizada a 700 °C indicou o maior valor a*. Além disso, os efeitos de diferentes quantidades relativas de constituintes também foram estudados. A temperatura e o tempo de aquecimento, volume de água e teor de fosfato afetaram a cor dos pigmentos.*

***Palavras-chave**: pigmento vermelho, minérios naturais, materiais de fosfato.*

INTRODUCTION

The use of harmful metals is being restricted worldwide by various government regulations in an attempt to reduce and control the environment pollution. However, the lack of alternatives necessitates the use of materials containing harmful metals in many fields [1, 2]. For example, inorganic color pigments with metals such as mercury, cadmium, and lead exhibit good properties, including high stability against radiation, heat resistance, coloring visibility, and low cost [3-5]. In addition, because of their low coloring and opacity, oxide pigments are not suitable for incorporation in paint and plastics [6]. Sulfate and nitrate pigments have lower heat resistance than oxide pigments and also 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 with suitable properties and facile production methods are demanded.

Several kinds of inorganic red pigments are available for use, e.g., red iron oxide, red lead, cadmium red, vermilion, and cinnabar [9-12]. However, they all suffer from several disadvantages. For instance, red iron oxide exhibits only limited colorfulness, while other pigments contain harmful metals such as lead, cadmium, and mercury. Therefore, a novel red pigment that is economical and does not contain any harmful metals is required. We focus on the natural ore natrophilite ($NaMnPO_4$), because it contains low-toxicity metals [13, 14]. Natural ores have high stability against radiation and heat resistance. Furthermore, they exist in solid phase, which allows applications in plastics, paint, ceramics, etc. Natrophilite contains bivalent manganese ion. The valence of manganese is important to prepare these novel red pigments. Here, novel inorganic red pigments $NaMnPO_4$, imitating natrophilite, were synthesized by heating a mixture of raw materials. The products were subsequently analyzed.

EXPERIMENTAL

Samples (2 g) imitating natrophilite ($NaMnPO_4$) were prepared as follows. Manganese carbonate was mixed with sodium dihydrogen phosphate through the following

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reaction:

$$MnCO_3 + NaH_2PO_4 \rightarrow NaMnPO_4 + CO_2 + H_2O \quad (A)$$

To improve the reaction, 5 mL water was added to the mixture and was left for 24 h. Subsequently, the mixture was heated between 400 and 800 °C for 1, 3, and 6 h. The volume of water was varied from 10 to 20 mL to determine its effect. To obtain the novel red pigment, similar compositions were studied through the following equations:

$$2NaH_2PO_4+2Na_2HPO_4+3MnCO_3 \rightarrow Na_6Mn_3(PO_4)_4 +3CO_2+3H_2O \quad (B)$$

$$2Na_2HPO_4+MnCO_3 \rightarrow Na_4Mn(PO_4)_2+ CO_2+H_2O \quad (C)$$

$$KH_2PO_4 + MnCO_3 \rightarrow KMnPO_4 + CO_2 + H_2O \quad (D)$$

$$2KH_2PO_4+2K_2HPO_4+3MnCO_3 \rightarrow K_6Mn_3(PO_4)_4+3CO_2+3H_2 \quad (E)$$

$$2K_2HPO_4+MnCO_3 \rightarrow K_4Mn(PO_4)_2+CO_2+H_2O \quad (F)$$

All chemicals were of commercial purity (Wako Chem. Ind., Osaka, Japan) and were used without further purification. The chemical compositions of these materials were determined by X-ray diffraction (XRD) analysis and infrared (IR) spectroscopy. The XRD patterns and IR spectra of the samples were recorded using an X-ray diffractometer (MiniFlex, Rigaku, Japan) with monochromatic CuKα radiation and an IR spectrometer (FT-IR 720, Horiba, Japan) using the KBr disk method, respectively. The color of the phosphate pigments was evaluated based on ultraviolet-visible (UV-vis) reflectance spectra (UV2100, Shimadzu, Japan; reference compound: $BaSO_4$). The color of the pigments was also described using a color analyzer (TES135 Plus, TES Electr. Electron., Taiwan). The L* value represents the whiteness of powder, in which 100 is white, while 0 is black. The a* value signifies the redness of the material, with positive (maximum +60) and negative (-60) values corresponding to red and green, respectively. The b* value denotes yellow intensity, in which positive (maximum +60) and negative (-60) values correspond to yellow and blue, respectively.

RESULTS AND DISCUSSION

Imitated $NaMnPO_4$: Fig. 1 shows the XRD patterns of the samples prepared at various temperatures. Samples heated at 500-800 °C indicated the peaks of $NaMnPO_4$. These peaks became narrow and evident on increasing the heating temperature. In contrast, the sample heated at 400 °C had ambiguous peaks. Therefore, the formation of $NaMnPO_4$ required heating at over 500 °C. Fig. 2 shows the IR spectra of the samples prepared at various temperatures. All samples had peaks at 560, 590, 610, 940, 1000, and 1060 cm^{-1}, corresponding to the phosphate anion. Samples

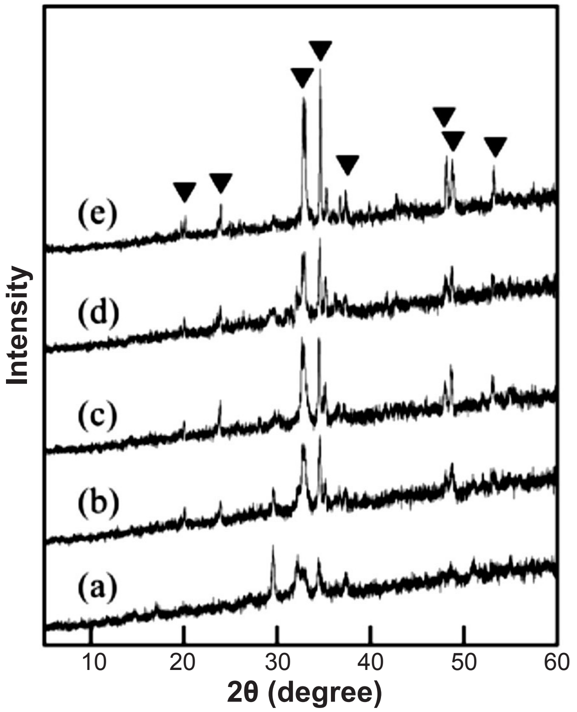

Figure 1: XRD patterns of samples prepared at various temperatures (for 1 h, with 5 mL water): a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C: ▼- $NaMnPO_4$.
[Figura 1: Difratogramas de raios X de amostras preparadas em diversas temperaturas (por 1 h, com 5 mL de água): a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; e e) 800 °C.]

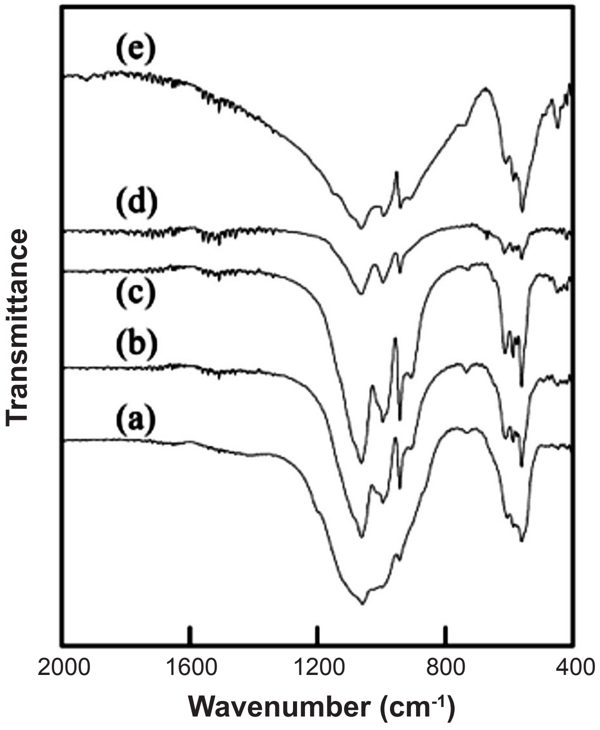

Figure 2: IR spectra of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).
[Figura 2: Espectros no infravermelho de amostras preparadas em: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; e e) 800 °C (por 1 h, com 5 mL de água.]

prepared at 500 and 600 °C contained small amounts of condensed phosphate indicated by a weak peak at 730 cm^{-1}, which was associated with P-O-P bonding [15]. However, heating at 700 °C removed this condensed phosphate.

Fig. 3 shows photographs of the samples prepared at various temperatures. The sample prepared at 400 °C resulted in a dark red powder. By heating at a higher temperature, the sample powder exhibited a lighter tone. The sample prepared at 800 °C resulted in yellowish dark red powder, different from other samples.

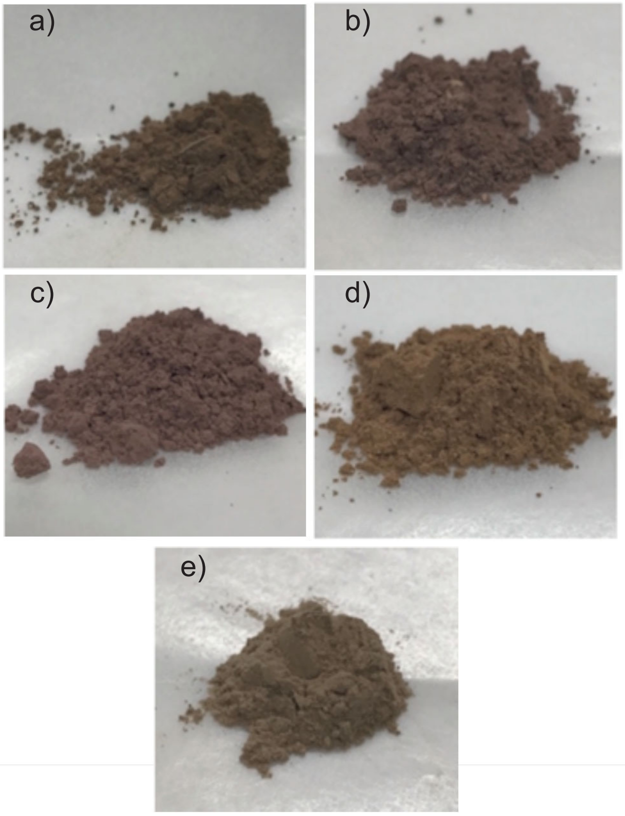

Figure 3: Photographs of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).

[Figura 3: Fotos das amostras preparadas em: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; e e) 800 °C (por 1 h, com 5 mL de água.]

Fig. 4 shows the UV-vis reflectance spectra of the samples prepared at various temperatures. The sample prepared at 400 °C produced the lowest reflectance. Moreover, the spectra of the samples prepared at 500 and 600 °C had a peak at 660 nm. A high reflectance at over 660 nm was observed in the spectrum of the sample prepared at 700 °C. However, the peak was absent in the sample prepared at 800 °C. Table I shows the L*a*b* values of the samples prepared at various temperatures. Samples prepared at higher temperatures produced a higher L* value corresponding to lightness. The sample heated at 700 °C had the highest a* value. The highest b* value was observed in the sample prepared at 800 °C, resulting in the yellowish powder shown in Fig. 3. By heating at 700 °C for 3 and 6 h, high values of a* and low L* were obtained. In addition, a larger volume of water produced higher a* values. However, samples prepared with 20 mL water had a low L* value. The heating temperature, time, and volume of water affected the color phase of the phosphate powders.

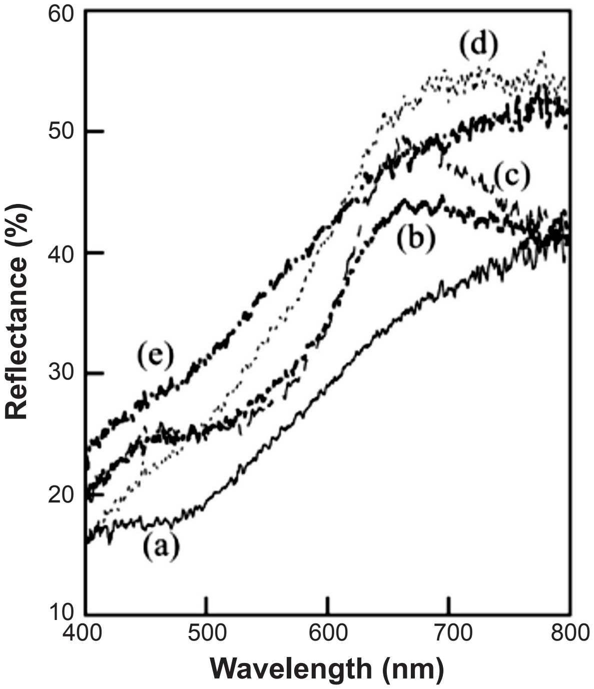

Figure 4: UV-vis reflectance spectra of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).

[Figura 4: Espectros de reflectância UV-vis das amostras preparadas em: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; e e) 800 °C (por 1 h, com 5 mL de água.]

Table I - Color of sample powders prepared under various conditions.

[Tabela I - Cor dos pós preparados em várias condições.]

Temp. (ºC)	Time (h)	Water content (mL)	L*	a*	b*
400	1	5	40.08	7.34	2.10
500	1	5	42.32	8.18	1.60
600	1	5	44.96	8.48	5.26
700	1	5	46.82	10.07	5.30
800	1	5	49.91	7.55	7.87
700	3	5	35.15	11.57	-0.41
700	6	5	35.51	11.65	-2.47
700	1	10	50.94	11.92	1.15
700	1	20	42.94	12.99	0.51

Other compositions: to obtain the novel red pigment, the effects of relative amounts of the constituents were also studied. High sodium and potassium ratios result in bright

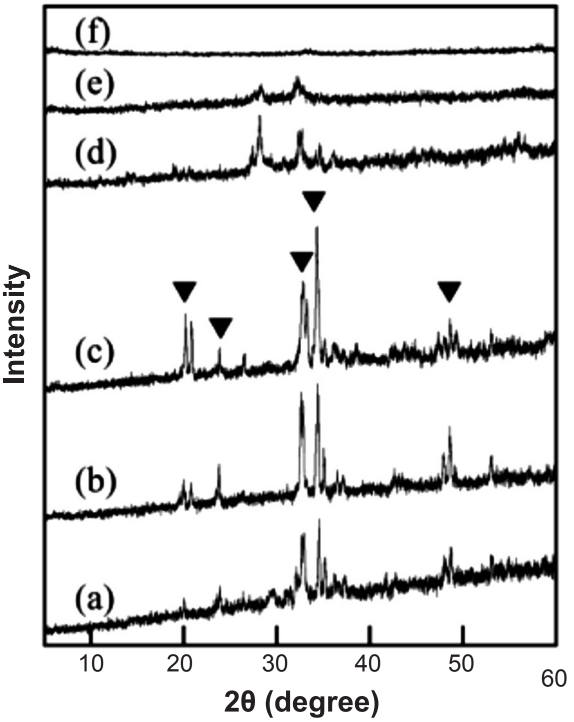

Figure 5: XRD patterns of samples prepared at 700 °C (1 h, 5 mL): a) $NaMnPO_4$; b) $Na_6Mn_3(PO_4)_4$; c) $Na_4Mn(PO_4)_2$; d) $KMnPO_4$; e) $K_6Mn_3(PO_4)_4$; and f) $K_4Mn(PO_4)_2$: ▼ - $NaMnPO_4$.
[Figura 5: Difratogramas de raios X de amostras preparadas a 700 °C (1 h, 5 mL): a) $NaMnPO_4$; b) $Na_6Mn_3(PO_4)_4$; c) $Na_4Mn(PO_4)_2$; d) $KMnPO_4$; e) $K_6Mn_3(PO_4)_4$; e f) $K_4Mn(PO_4)_2$.]

Table II - Color of sample powders prepared in various Na/Mn and K/Mn ratios (at 700 °C, for 1 h, with 5 mL water).
[Tabela II - Cor dos pós preparados nas várias razões Na/Mn e K/Mn (a 700 °C, por 1 h, com 5 mL de água).]

Molar ratio	Composition	L*	a*	b*
Na/Mn=1/1	$NaMnPO_4$	46.82	10.07	5.30
Na/Mn=2/1	$Na_6Mn_3(PO_4)_4$	57.23	8.65	14.57
Na/Mn=4/1	$Na_4Mn(PO_4)_2$	45.40	9.85	11.32
K/Mn=1/1	$KMnPO_4$	40.60	2.30	9.02
K/Mn=2/1	$K_6Mn_3(PO_4)_4$	22.60	7.40	7.96
K/Mn=4/1	$K_4Mn(PO_4)_2$	18.07	3.72	3.51

sample powders because sodium and potassium compounds easily form colorless materials. Fig. 5 shows the XRD patterns of the samples prepared with various Na/Mn and K/Mn ratios. Samples prepared with sodium salts presented the peaks of $NaMnPO_4$. These peaks became more evident with increasing sodium ratio. Additionally, samples prepared with K/Mn= 1/1 and 2/1 had weak ambiguous peaks. Potassium salt produced different crystal structures with sodium salt. The sample prepared with K/Mn= 4/1 was in amorphous state.

Table II shows the L*a*b* values of phosphate materials prepared in various Na/Mn and K/Mn ratios. Samples prepared with Na/Mn= 2/1 and 4/1 had lower a* values and higher b* values than the sample prepared with Na/Mn= 1/1. Samples prepared with potassium salts indicated low L* values. Samples prepared with high sodium ratio and potassium salt never exhibited high L* and a* values.

CONCLUSIONS

Novel red phosphate pigments imitating natrophilite were obtained by heating a mixture of manganese carbonate with various phosphates. Samples prepared over 500 °C indicated an XRD pattern associated with $NaMnPO_4$. The sample powder color became light when heated at a higher temperature. The UV-vis reflectance spectra of the samples prepared at 500 and 600 °C had a peak at 660 nm. A high reflectance at over 660 nm was observed in the spectrum of the sample prepared at 700 °C. The suitable condition to obtain high L* (lightness) and a* (redness) values is heating at 700 °C for 1 h with 5 or 10 mL of water (for 2 g sample). Samples prepared with potassium salt became dark powders.

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