Journal of Materials Science and Engineering B 9 (1-2) (2019) 1-5
doi: 10.17265/2161-6221/2019.1-2.001

Synthesis of Novel Dark Red Phosphate Pigments in Imitation of Natural Ore

Hiroaki Onoda and Syohei Fujikado

Department of Informatics and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-cyo, Sakyo-ku, Kyoto 606-8522, Japan

Abstract: As novel dark red pigment, sodium manganese phosphate, $NaMnPO_4$, imitated with Natrophilite, was synthesized by heating at various conditions. The heating temperature and time, volume of water, phosphorus resource were studied in this process. 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. Further, similar chemical compositions with $NaMnPO_4$ were also studied in the same method. The obtained samples had weak peaks of $NaMnPO_4$ in XRD patterns. Sample synthesized in Na/Mn = 1/1 at 700 ºC for 6 hours indicated high redness, a* value.

Key words: Dark red pigment, natural ores, phosphate materials.

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 red pigments, for example, that are available for use, red iron oxide, red lead, cadmium red, vermilion, cinnabar and so on [9-12]. However, they have some problems, there is a limited colorfulness of red iron oxide. Other pigments include harmful metals, lead, cadmium, and mercury. Therefore, novel red pigment without precious and harmful metals is required. We focus on the natural ore, Natrophilite, $NaMnPO_4$, because this ore has only low toxicity 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. Manganese ion is bivalent in Natrophilite. The valence of manganese is important to prepare the novel red pigments imitated with these ores.

In this work, novel inorganic red pigments imitated with natural ores, $NaMnPO_4$, were synthesized by heating the mixture of powder manganese and some kinds of phosphates and then estimated from the viewpoint of pigment.

2. Experimental

Sample (2 g) imitated of Natrophillite, $NaMnPO_4$, was prepared as follows. Manganese powder was mixed with sodium di-hydrogen phosphate in the

Corresponding author: Hiroaki Onoda, associate professor, research fields: inorganic material, pigment, environmental science.

following reaction:

$$Mn + NaH_2PO_4 \rightarrow NaMnPO_4 + H_2 \quad (1)$$

To improve the react, 5 mL of water was added to the mixture, and then let stand for 1 day. The mixture was heated at 400-800 ºC for 1, 3, and 6 hours. Further, the volume of water changed to 10 or 20 mL to react more homogenously.

To obtain the novel red pigment, the similar compositions were studied in the following equations.

$$2NaH_2PO_4 + 2Na_2HPO_4 + 3Mn \rightarrow Na_6Mn_3(PO_4)_4 + 3H_2 \quad (2)$$

$$2Na_2HPO_4 + Mn \rightarrow Na_4Mn(PO_4)_2 + H_2 \quad (3)$$

$$KH_2PO_4 + Mn \rightarrow KMnPO_4 + H_2 \quad (4)$$

$$2KH_2PO_4 + 2K_2HPO_4 + 3Mn \rightarrow K_6Mn_3(PO_4)_4 + 3H_2 \quad (5)$$

$$2K_2HPO_4 + Mn \rightarrow K_4Mn(PO_4)_2 + H_2 \quad (6)$$

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 $NaMnPO_4$ Composition

Fig. 1 shows XRD patterns of the samples synthesized at various temperatures. All samples exhibited low-intensity peaks of $NaMnPO_4$. These peaks became intense with the increase of heating temperature. The peak at approximately 29° was attributed to MnO_2. A part of manganese got converted to MnO_2 by heating under air. The formation of MnO_2 was expected to influence the color of the materials. Because MnO_2 is black, the suppression of this formation is important to obtain brilliant color of pigments. Fig. 2 shows IR spectra of the samples synthesized at various temperatures. All samples exhibited absorption peaks at 550, 910, and 1,100 cm^{-1}, due to the presence of phosphate anions. The intensity of the peak at 910 cm^{-1} increased with increasing heating temperature. IR spectra of the samples heated at 500 and 600 °C exhibited a peak at 740 cm^{-1} attributed to the formation of a P-O-P bond.

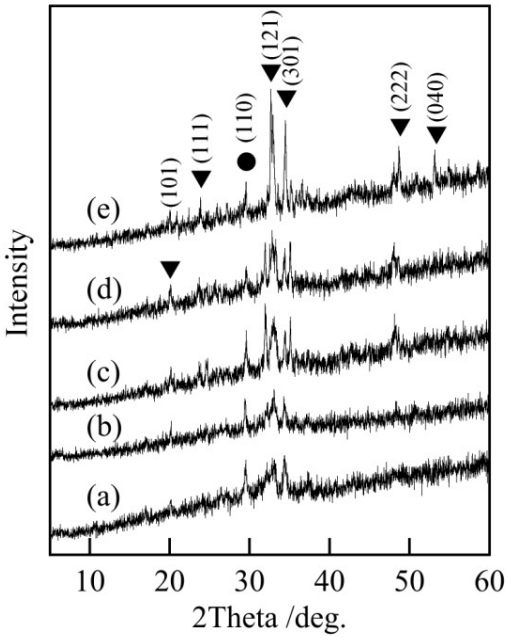

Fig. 1 XRD patterns of samples prepared at various temperatures (1 hour, 5 mL): (a) 400ºC; (b) 500 ºC; (c) 600 ºC; (d) 700 ºC; (e) 800 ºC. ▼; $NaMnPO_4$, ●; MnO_2.

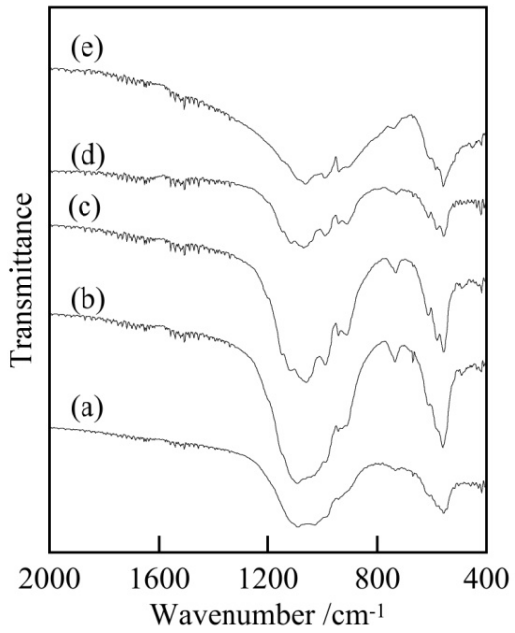

Fig. 2 IR spectra of samples prepared at various temperatures: (a) 400 ºC; (b) 500 ºC; (c) 600 ºC; (d) 700 ºC; (e) 800 ºC (1 hour, 5 mL).

A small amount of condensed phosphate was formed at 500 and 600 °C, and decomposed at 700 °C [15]. The heating temperature had little influence on the chemical composition of these phosphate pigments.

Fig. 3 shows images of the samples prepared at various temperatures. All samples were brownish-red powders. The sample became darker when heated to higher temperatures. Fig. 4 shows the UV-vis reflectance spectra of the samples prepared at various temperatures. Samples synthesized at higher temperatures exhibited lower reflectance, which corresponded to the extent of the samples' darkness. A low-intensity peak at approximately 700 nm was observed in the reflectance spectra of samples synthesized at 600 and 700 °C; this peak disappeared at 800 °C. Table 1 shows the L*a*b* values of the sample powders prepared under various conditions. The L* values decreased with increasing temperature; this agreed well with the data from the UV-Vis reflectance spectra. Samples synthesized at 600 and 700 °C presented higher a* values and redness than other samples. After heating for many hours, the powder sample presented a lower L* value, signifying

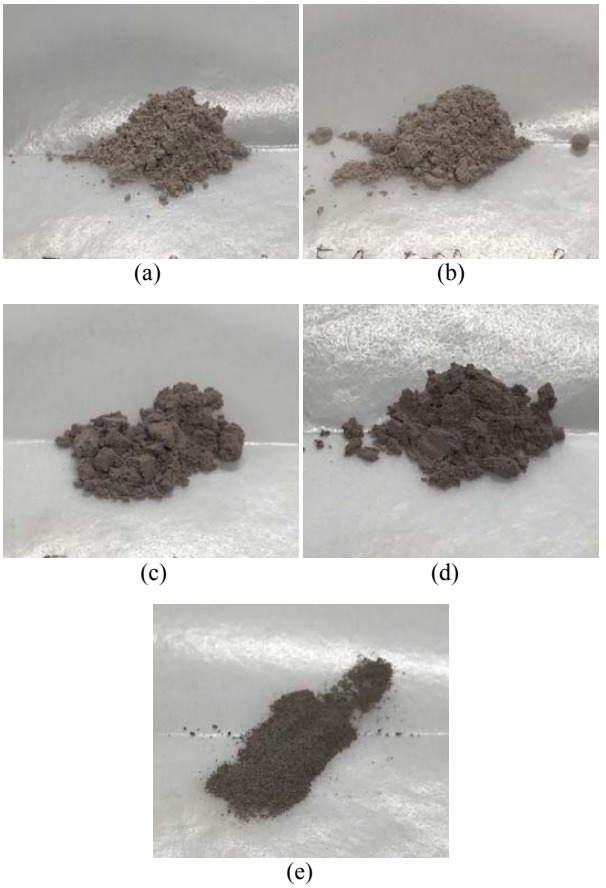

Fig. 3 Photographs of samples prepared at various temperatures: (a) 400 ºC; (b) 500 ºC; (c) 600 ºC; (d) 700 ºC; (e) 800 ºC (1 hour, 5 mL).

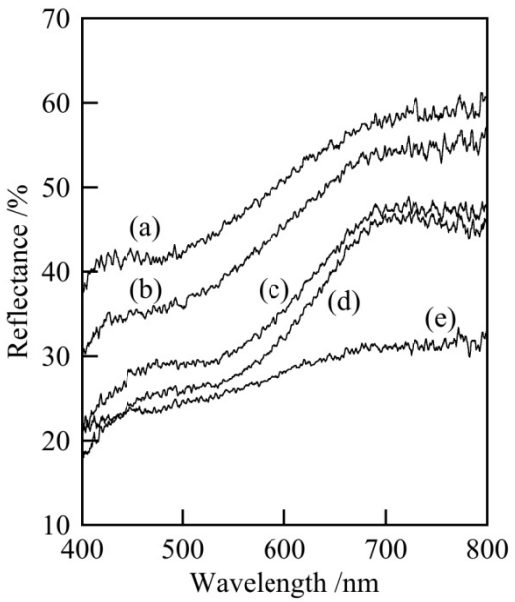

Fig. 4 UV-Vis. reflectance spectra of samples prepared at various temperatures: (a) 400 ºC; (b) 500 ºC; (c) 600 ºC; (d) 700 ºC; (e) 800 ºC (1 hour, 5 mL).

Table 1 Color of sample powders.

Temp. /ºC	Time /hour	Water /mL	L*	a*	b*
400	1	5	70.75	4.29	7.01
500	1	5	68.26	5.74	8.26
600	1	5	67.46	7.36	7.27
700	1	5	65.20	9.97	7.44
800	1	5	51.43	4.74	7.48
700	3	5	55.33	11.18	7.98
700	6	5	54.09	13.92	7.34
700	1	10	60.72	14.32	7.41
700	1	20	59.20	14.71	6.77

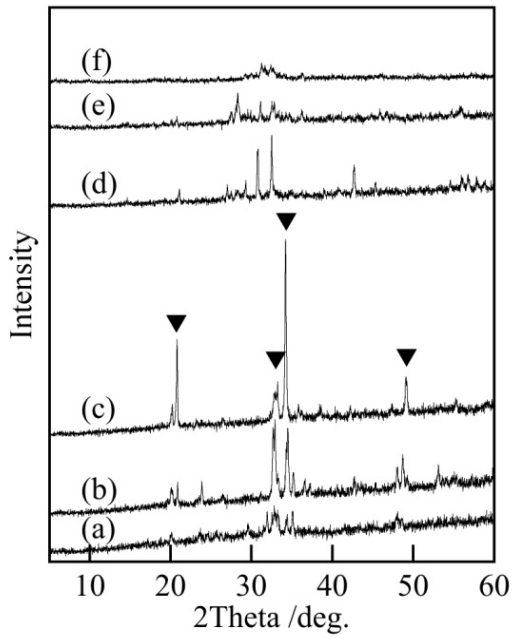

Fig. 5 XRD patterns of samples prepared at 700 ºC (1 h, 5 mL): (a) Na/Mn=1/1; (b) 2/1; (c) 4/1; (d) K/Mn=1/1; (e) 2/1; (f) 4/1. ▼: $NaMnPO_4$.

Table 2 Color of sample powders (700 ºC, 1 h, 5 mL).

	Composition	L*	a*	b*
Na/Mn=1/1	$NaMnPO_4$	65.20	9.97	7.44
Na/Mn=2/1	$Na_6Mn_3(PO_4)_4$	79.50	4.90	8.71
Na/Mn=4/1	$Na_4Mn(PO_4)_2$	61.05	4.70	4.89
K/Mn=1/1	$KMnPO_4$	53.87	8.97	12.09
K/Mn=2/1	$K_6Mn_3(PO_4)_4$	49.56	9.81	12.83
K/Mn=4/1	$K_4Mn(PO_4)_2$	36.03	7.62	10.14

darkness. By adding more water, the redness of the sample improved. The b* values exhibited little difference with the heating temperature, time, and volume of water. It is difficult to obtain high a* value of samples as a novel red pigment. Further study, for example the additives, and so on, is required to obtain high a* value.

3.2 Other Compositions

To obtain a novel red pigment, evaluations were also performed for compositions similar to $NaMnPO_4$. Fig. 5 shows XRD patterns of the samples prepared at various Na/Mn and K/Mn ratios. The sample prepared at Na/Mn = 4/1 exhibited strong peaks of $NaMnPO_4$ (Fig. 5c). Peaks at 21.1°, 30.8°, 32.5°, and 42.8° were observed in the XRD pattern of the sample prepared at K/Mn = 1/1 (Fig. 5d). However, these peak values were different for the sample with sodium salts. Nevertheless, the peak pattern was similar to that of $NaMnPO_4$. Samples prepared at K/Mn = 2/1 and 4/1 exhibited unknown weak peaks (Figs. 5e and 5f).

Table 2 shows the L*a*b* values of the samples prepared at various Na/Mn and K/Mn ratios. Samples synthesized with a high sodium ratio presented a lower a* value than those prepared at Na/Mn = 1/1. Because a high sodium ratio implies a low manganese ratio in the sample, the phosphate powder loses its redness. Further, potassium manganese phosphates presented low L* and high b* values. Therefore, these high-sodium and potassium salts were unsuitable as a novel red pigment.

4. Conclusions

Novel dark red phosphate pigments imitating Natrophillite were synthesized from manganese powder and other phosphates. The synthesized samples exhibited weak peaks of $NaMnPO_4$ in the XRD patterns. Samples synthesized at 600 and 700 °C had higher a* values, and more redness as compared to other samples. By heating for a long duration, the samples became darker. Evaluations were also carried out for compositions similar to $NaMnPO_4$ using the same methods. Overall, the sample synthesized using Na/Mn = 1/1, at 700 °C for 6 h, presented a high redness and high a* value.

References

[1] Amat, A., Millani, C., and Fantacci, S. 2016. "Structual and Electronic Properties of the $PbCrO_4$ Chrome Yellow Pigment and of Its Light Sensitive Sulfate-substituted Compounds." *RSC Adv.* 6: 36336-44.

[2] Tao, Z., Zhang, W., Huang, Y., Wei, D., and Seo, H. J. 2014. "A Novel Pyrophosphate $BaCr_2(P_2O_7)_2$ as Green Pigment with High NIR Solar Reflectance and Durable Chemically Stability." *Solid State Sci.* 34: 78-84.

[3] Radepont, M., Conquinot, Y., Janssens, K., Ezrati, J.-J., and Cotte, M. 2015. "Thermodynamic and Experimental Study on the Degradation of the Red Pigment Mercury Sulfide." *J. Anal. At. Spectrom.* 30: 599-612.

[4] Rosi, F., Grazia, C., Gabrieli, F., Romani, A., Paolantoni, M., Vivani, R., Brunetti, B. G., Colomban, P., and Miliani, C. 2016. "UV-Vis-NIR and Micro Raman Spectroscopies for the Non Destructive Identification of $Cd_{1-x}Zn_xS$ Solid Solutions in Cadmium Yellow Pigments." *Microchem. J.* 124: 856-67.

[5] Li, M., Wand, J., and Ma, Q. 2015. "The Effect of Lead Additives on Ancient Chinese Purple Pigment Synthesis." *J. Cultural Heritage* 16 (4): 575-8.

[6] Jiang, S., Peng, L., Guo, R., Miao, D., Shang, S., Xu, J., and Li, A. 2016, "Preparation and Characterization of Fe_2O_3 Coating on Quarts Fabric by Electron Beam Evaporation." *Ceram. Intern.* 42 (16): 19386-92.

[7] Migurei, C., Pinto, J. V., Clarke, M., and Melo, M. J. 2014. "The Alchemy of Red Mercury Sulphide: The Production of Vermillion for Medieval Art." *Dyes Pig.* 102: 210-7.

[8] Ohashi, M., Kusumoto, K., Sugiyama, T., and Kato, K. 2016. "Influence of Nitrides on Synthesis of Tantalum (V) Oxynitride TaON by Heat Treatment without Flowing Ammonia." *J. Ceram. Soc. Jpn.* 124 (9): 959-62.

[9] Ryan, M. J., Kney, A. D., and Carley, T. L. 2017. "A Study of Selective Precipitation Techniques Used to Recover Refined Iron Oxide Pigments for the Production of Paint from a Synthetic Acid Mine Drainage Solution." *Appl. Geochem.* 79: 27-35.

[10] Brokbartold, M., Temminghoff, E. J. M., Weng, L., and Marschner, B. 2013, "Unique Characteristics of Pb in Soil Contaminated by Red Lead Anti-corrosion Paint." *Soil Sedim. Contam.* 22: 839-55.

[11] Botteon, A., Conti, C., Realini, M., Colombo, C., and Matousek, P. 2017. "Discovering Hidden Painted Images: Subsurface Imaging Using Microscale Spatially Offset Raman Spectroscopy." *Anal. Chem.* 89: 792-8.

[12] Radepont, M., Coquinot, Y., Janssens, K., Ezrati, J., Nolf, W., and Cotte, M. 2015. "Thermodynamic and Experimental Study of the Degradation of the Red Pigment Mercury Sulfide." *J. Anal. Atom. Spectrom.* 30: 599-612.

[13] Vignola, P., Hatert, F., Fransolet, A., Medenbach, O., Diella, V., and Ando, S. 2013. "Karenwebberite, $Na(Fe^{2+},Mn^{2+})PO_4$, a New Member of the Triphylite Group from the Malpensata Pegmatite, Lecco Province, Italy." *J. Earth Planet. Mater.* 98 (4): 767-72.

[14] Grave, E. D., Costa, G. M., Alboom, A. V., and Vandenberghe, R. E. 2013. "Low-temperature Mössbauer Study of Heterosite, $(Fe, Mn)PO_4$." *Spectrochim. Acta* 100: 104-8.

[15] Mulongo-Masamba, R., Kassri, T. E., Khachani, M., Arsalane, S., Halim, M., and Hamidi, A. E. 2016. "Synthesis and Thermal Dehydroxylation Kinetic of Anhydrous Calcium Phosphate Monetite $CaHPO_4$." *J. Therm. Anal. Calorim.* 124: 171-80.