Maëva GUILLOT
Sorbonne University
M1 Chemistry- Physics et Chemistry of Materials (PCMat)
Internship 2022- from April 15th to August 31st - Okayama University - JAPAN

Micro/nano structures and color tones of hematite nano-particles for beautiful, highly bright, sustainable and heat-resistant red pigments

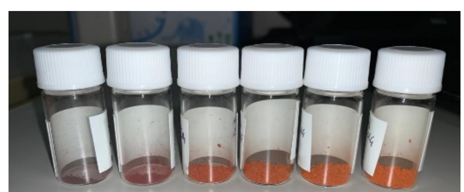
This internship takes place in the laboratory of Professor FUJII Tatsuo, in the department of Applied Chemistry in the Graduate School of Natural Science and Technology-Okayama University.

Gathering with students of the laboratory

The topic is focused on the improvement of red pigments, and more specifically on hematite, α-Fe_2O_3, which is the most common red pigment used since ages, likely because hematite is the most stable iron oxide on earth.

In Japan, pigments are part of the paintings culture especially in Ukiyo-e paintings. Red pigment and more precisely hematite has been particularly present over ages. It can be found into BIZEN wares with red-brownish shades, but also in Fukiya village, a remote rural district in the hills of Takahashi City, about 100kilometers north of Okayama, where the red color of walls and roofs is due to hematite. Pigments are called Bengara pigments.

The colour of hematite is red, sometimes deep dark and tends to tarnish over time. Here, one aim is to get highly bright and sustainable red pigment so that it can be applied in paintings. The paintings should also be heat-resistant not only to resist high temperatures during Japan's summer, but also in a vision of using less energy, especially regarding the Global Warming which is a current issue.

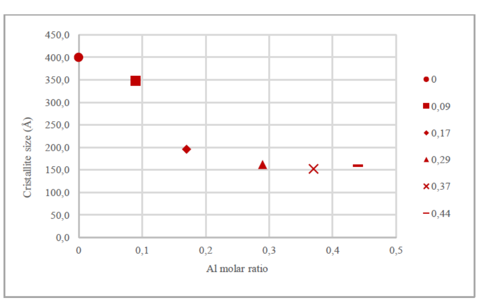


Range of composition: From 0 Al to 0,5 Al added, obtained at 1000°C

To achieve that goal, it was planned to:

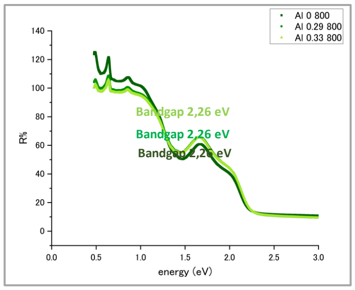
a - modulate the hematite composition by doping it with Al or Si
b - adapt synthesis conditions and so the shape of hematite particles.

When pigments particles are synthetized, there are analyzed thanks to different techniques, such as X-ray diffraction (DRX), Scanning electron microscopy (SEM), X-ray fluorescence (XRF), a spectrophotometer, Optical reflectance, and so on. Each technique is necessary to determine and check the composition, the shape of particles, the size of crystallites, but also to have the lattice parameters, and information about colors (redness, yellowness, brightness).

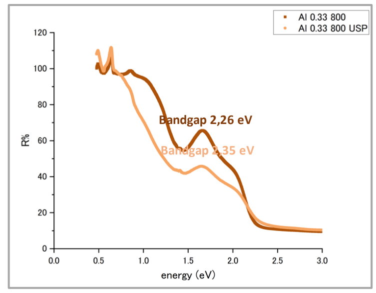


Crystallite size as a function of Al molar ratio (samples heated at 800°C)

For that matter, Al is added to hematite to lighten up the color of the sample. Two different techniques have been used to synthetize the pigments particles. First a precipitation method was used and the particles shape obtained was fibrous. There, samples were either heated to 800°C either to 1000°C. In these two cases, we obtained quite different colors for same composition of Al. The second method used is the ultrasonic spray pyrolysis (USP), which consists in making spherical particles thanks to ultrasonic waves for different compositions, as did before. Here, an impact of the particles shape is also observed. Upon increasing the Al amount which lighten the hematite colour, the size of the crystallite size decreases. The lattice constants also decreased, so the exchange integral between atomic orbitals increased. Then the bandgap is expected to get larger when the amount of Al gets bigger. The spherical shape was increasing the bandgap of hematite samples.

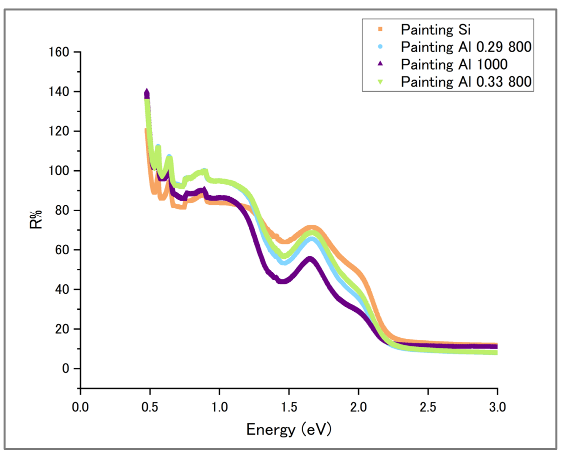


Optical reflectance spectra of samples heated at 800°C

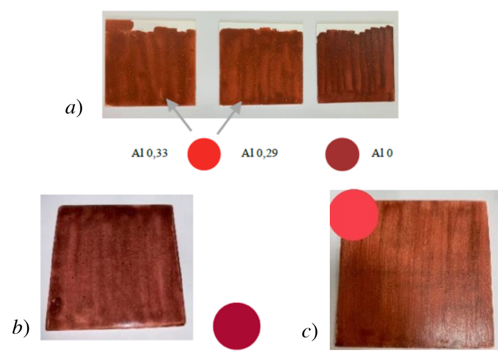


Optical reflectance spectra of same composition samples with different shapes

Si was also added to the composition. There, the brighter sample was obtained for a molar ratio of 0,1 Si. Samples were less pure with Si as well but the reflectance in visible light was very high. All brighter samples were tested into paintings, and it appeared that the highest reflectance into the infra-red region was obtained for 0,33 Al heated at 800°C. This was the most promising painting for application as heat-resistant pigment.



Optical reflectance spectra of paintings done with the brightest samples



Application in paintings for the lightest samples doped either with Al either with Si:

- *a) Paintings done with Al-hematite heated at 800°C*
- *b) Paintings done with 0,41 Al heated at 1000°C*
- *c) Painting done with 0,1 Si heated at 800°C*