The Synthesis and Spectroscopic Investigations of Ancient Chinese Pigments

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Abstract

A Raman microscope was built in order to study Chinese purple ($BaCuSi_2O_6$) and Chinese Blue ($BaCuSi_4O_{10}$). A thermocouple oven was used to synthesize the pigments. Attenuated total reflection (ATR) and photoacoustic were used in conjunction with FT-IR to analyze the products.

Introduction

Chinese Purple and Chinese Blue are barium copper silicates that were found on the terracotta warriors in Xi'an (西安), China. These pigments have been found on artifacts dating back to the Warring States period (500 BCE)[1]. Although they have been in production for thousands of years, these pigments have been difficult to synthesize in the modern era. Chinese Purple is thermally unstable (breaks down above ~1200°C) and requires high temperatures to synthesize (900-1100°C)[1]. This pigment was discovered after Chinese glass-making and glazes, all three of which have similar ingredients such as barium and lead oxide. The introduction of color to glazes may have lead to the discovery of this pigment[2].

Raman microscopy has been used to study these pigments. Raman microscopy is an analytical technique used to study molecules. It works by using a laser as a light source, whose photons collide with a sample, releasing three types of radiation: Stokes, anti-Stokes and Rayleigh. It is nondestructive and generally does not have water interference, making it ideal for identifying pigments in ancient artifacts[3].

Raman spectrometers, while useful, are expensive. Raman microscopes are even more expensive than their spectrometer counterparts. However, the instruments themselves are not complicated. In theory, it is possible to create a Raman microscope out of simple laboratory parts such as old microscopes and lenses. While several parts are available in the lab, others are not. It is possible to create parts out of aluminum, wood and other common workshop materials, but it is not convenient for smaller, more detailed parts. With the introduction of 3D printing, creating these small parts has become easier. Creating a more precise and small part, such as a NDBS mount (Figure 3) is easy with 3D printing.

3D printing works by using a filament (plastic, metal, carbon fibers, wood and etcetera) that is fed into an extruder, which becomes hot, melting the filament and placing it on a warm plate. The extruder moves, placing the melted pigment over the plate in a pattern outlined by a CAD program[4].

Figure 1. The pigments preheated (top row) and after heating (bottom row). From left to right: Sample A, Sample B, Sample C

Table 1. Sample Reactants and Ratios

Sample	Reactants	Ratio
A	Witherite, malachite, silica	1:2:8 (+5% PbO)
B	Witherite, copper oxide, silica	1:1:2
C	Witherite, copper oxide, silica	1:1:2 (+5% PbO)

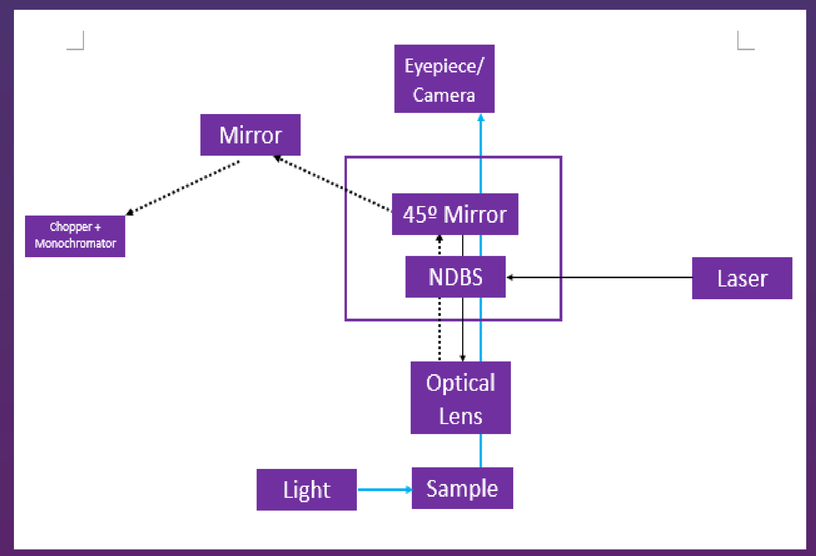

Figure 2. Optical Diagram of Raman Microscope

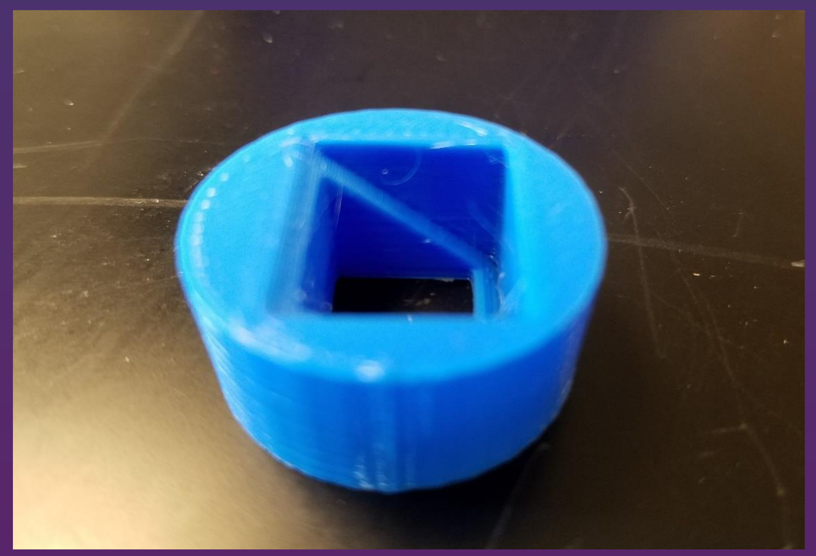

Figure 3. Picture of the 3D printed notch dichroic beam splitter mount

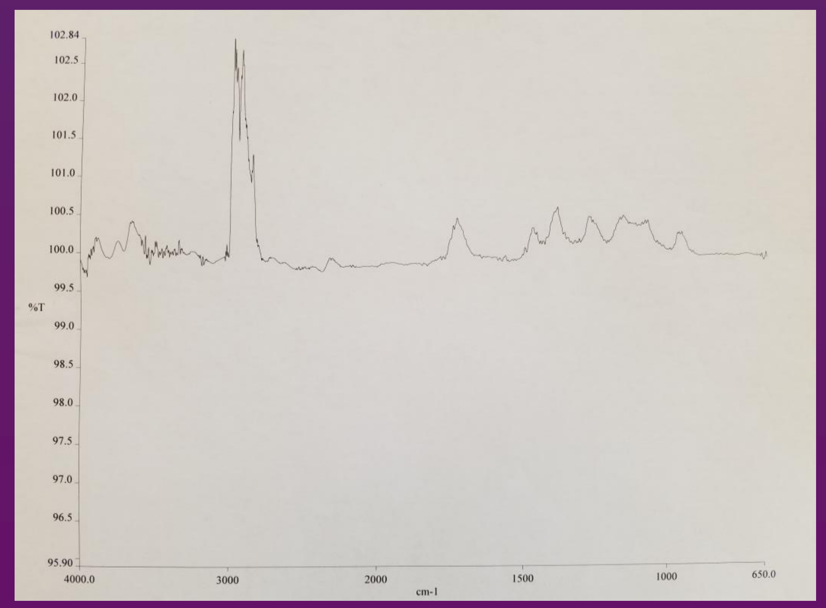

Figure 4. ATR Spectra of Sample C

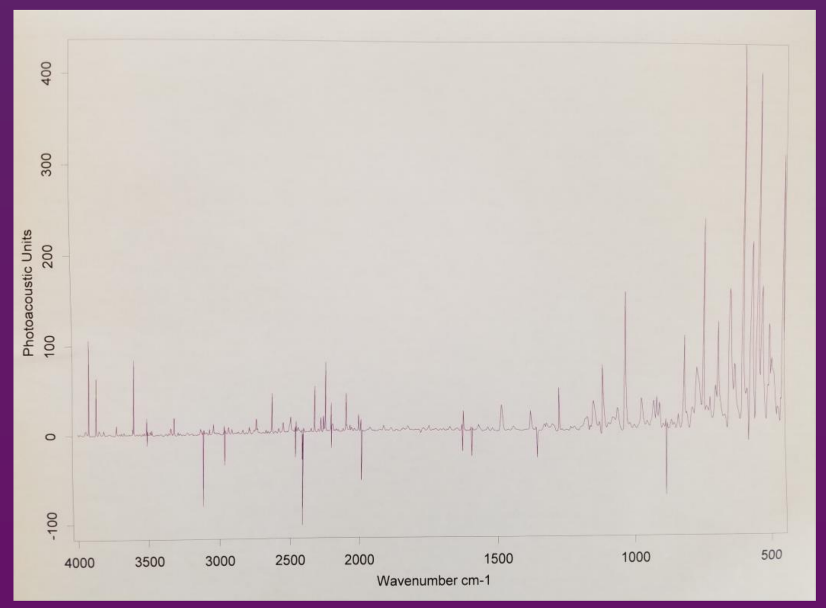

Figure 4. Photoacoustic Spectra of Sample C

Results and Discussion

- Three samples were synthesized: Sample A, Sample B and Sample C
- Sample A's resulting color after heating was a blue.
- Sample B's resulting color after heating was a gray.
- Sample C 's resulting color after heating was a mix of purple and blue-gray
- Samples B and C had strong peaks at 3000 cm^{-1} and ~1650 cm^{-1} in their ATR spectra
- Sample A had a peak at 3000 cm^{-1} and at ~800 cm^{-1}
- All three samples had a double peak at ~3900 cm^{-1} and several small peaks between 2000 cm^{-1} and 3000 cm^{-1} in their photoacoustic spectra
- Samples A and C had a cluster of peaks around 500 cm^{-1}, but B did not

Conclusion

- View Sample Using Eyepieces and Camera
- 3D Printed Part Successfully
- Reflect Light onto monochromator through microscope and sample
- The three samples seem to have been contaminated with carbon
- The peaks around 1000 cm^{-1} correlate to silicon derivatives
- Further research will include programming the microscope and analyzing the samples with it.
- Samples should be analyzed with NIR instead of FT-IR/ATR

References

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