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Characterization of photoluminescent and Raman properties of ultramarine blue pigment variants with a novel multimodal approach

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Abstract. Ultramarine Blue (UB) pigment, derived from lapis lazuli, holds a significant place in the history of late medieval and Renaissance Europe, owing to its unusually bright colour and stability. Its prohibitive price, which equalled that of gold, meant that it was only used by estimated artists. In this work we present a non-invasive, multimodal approach to the characterization of the photoluminescent properties of different variants of the pigment. The ultimate goal of this research is to propose a protocol for the identification of UB in artworks thanks to the combination of Raman spectroscopy and time resolved-photoluminescence spectroscopy and imaging.

1 Introduction

Ultramarine blue is notorious for being one of the most expensive blue pigments in medieval and Renaissance Europe, due to its remote geographical origin (quarries were in Afghani mountains) and laborious method of extraction devised by Cennino Cennini. The price of ultramarine blue led to it only being employed by the most renowned artists and for the most important religious iconographic figures, such as for the robes of Christ and Mary, or for the skies of religious scenes [1].

The study of Cultural Heritage is always in need of techniques that can preserve the artifacts as much as possible by minimizing damage to the decorated surfaces or sample extraction.

In this work, we present a novel and multimodal approach to study ultramarine blue pigments with non-invasive techniques, which include Raman spectroscopy and time resolved photoluminescence spectroscopy and imaging.

Characterizing the photoluminescent properties of this pigment is paramount to understand the possibility of detecting its presence in artworks non-invasively with a multi-analytical approach including fluorescence studies.

2 Materials and Methods

The samples we analysed were purchased from the company Kremer Pigmente©. They consisted of ultramarine blue pigments of different qualities, provenances and extraction methods.

Samples were first prepared as bulk to study their mean fluorescence properties and chemical composition: for the purpose pigments were collected in small wells. Secondly, pigment depositions were achieved by diluting a minimal quantity of pigment with a drop water, which was placed on a metallic support where it dried out in a controlled atmosphere. The result was a deposition of powder with well separated grains, which were also well adhered to the support surface. This second type of samples allowed us to infer the fluorescence properties of individual grains in each sample and relate them with the chemical identification of individual grains provided by Raman spectroscopy.

In the following, we present an overview of the techniques used to study the samples.

2.1 Time Resolved Photoluminescence (TRPL) spectroscopy

Optically induced emission from bulk samples was studied with a time-resolved gated detector coupled to a spectrometer following pulsed laser excitation at 355 nm. Time-gated spectra of the emission from samples occurring at different timescales allowed us to identify different types of emitters with variable relative concentration depending on quality of the pigment.

2.2 Optical Microscopy (OM)

Samples prepared as powder dispersions were first observed under UV light to have a qualitative overview of the fluorescent grains and select regions of interest within the powder dispersion with the most intense or diverse collection of fluorescent species. These regions of interest were then analysed in terms of spectral and decay kinetic fluorescence properties with the setups described in section 2.3 and 2.4.

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2.3 Fluorescence Lifetime Imaging (FLIM)

Fluorescence from samples was excited with the same 355 nm pulsed laser source as before and imaged with a time-gated image intensifier. By collecting a sequence of images of the emission at different delays with respect to pulsed excitation, this technique allowed us to measure the decay of the fluorescence emission of selected grains and reconstruct their emission lifetime.

2.4 Time-Gated Hyperspectral Imaging (TG-HSI)

The same setup employed in the FLIM technique, with the addition of the TWINS interferometer placed in front of the time-gated image intensifier [2], allowed us to observe the spectral properties of the emission at different timescales and to reconstruct the time-gated emission spectra of individual grains in samples.

2.5 Raman spectroscopy

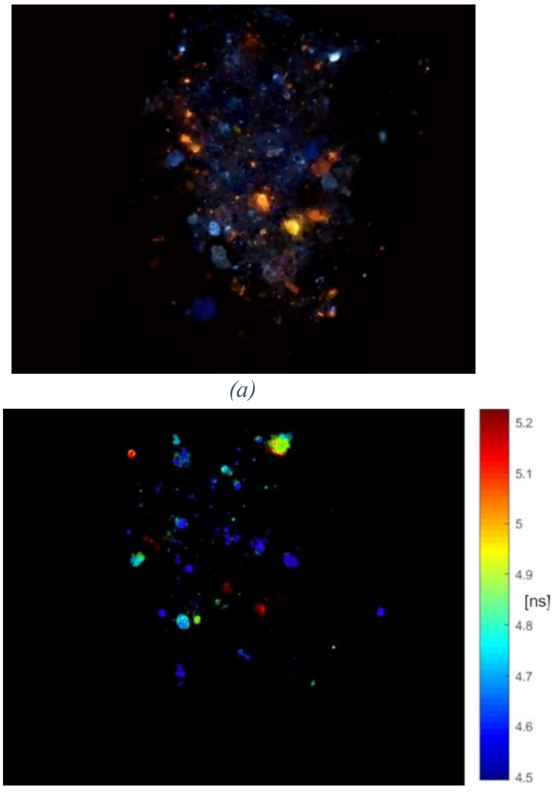
A 785 nm and 532 nm laser source has been used to chemically characterize the different chemical species and impurities in UB through their specific Raman peaks.

3 Results

The study of optical emission from samples highlighted the presence of different fluorescent species, which differ both in emission spectrum and lifetime. Indeed, while lazurite blue grains - the primary mineral responsible for the blue coloration of lapis lazuli - do not display any fluorescent emission, many other grains, which occur in the pigment as impurities with different relative concentrations depending on the pigment quality and provenance, are fluorescent. Specifically, we identified three main classes of fluorescence emitters: blue emitters, yellow and orange emitters and IR emitters. Analyses carried out with Raman spectroscopy on the same fluorescent grains allowed us to chemically identify most of them by comparing the experimentally obtained spectra with literature.

Blue emitters are most likely diopside. Their emission spectrum peaks between 430 and 460 nm and their lifetime is of around 5 nanoseconds. Yellow and orange emitters have a spectrum peaking between 550 and 650 nm and have a much longer lifetime in the order of microseconds (of around 1 to 10 microseconds). They appear to be silicates characterized by the sodalite cage structure. IR-emitters give rise to a band in the 720-800 nm range and present the longest lifetimes of tens of microseconds. Most of these fluorescent grains appear white or colorless under visible light. However, a portion of the yellow-orange fluorescent emitters are blue. Thanks to their characteristic peak at 548 cm^{-1}, we have confirmed them to be a blue-coloured hauyne, a mineral belonging to the same family as lazurite (sodalites).

Figure 1 (a), taken with an optical microscope and UV illumination, shows the variety of fluorescent grains in a sample. In Figure 1 (b) the hue of the grains represents the lifetime of the fluorescent emission. One can clearly appreciate the difference in lifetime among the blue emitting species (appearing as blue and green, which corresponds to having a lifetime of 4 to 5 ns) and the yellow-orange emitting species, which are coloured deep red, representing a much longer lifetime.



(a)

(b)

Fig 1. (a) UB sample examined under UV light and (b) same region of interest analysed with the FLIM technique. The hue of the grains in this false colour image represents the effective lifetime of the fluorescent emission.

4 Conclusion

In conclusion, we have managed to characterize the distinct fluorescent emission of the ultramarine blue pigment and have succeeded in identifying most of the emitters thanks to Raman spectroscopy. This non-invasive multimodal approach is promising for the detection of the pigment in artworks.

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