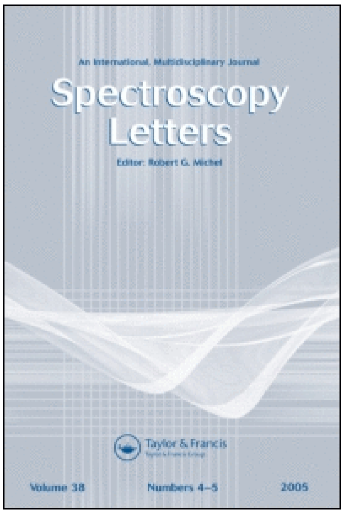

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Zelliges from Dar-El Beïda Palace in Meknes (Morocco): Optical Absorption and Raman Spectrometry

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Zelliges from Dar-El Beïda Palace in Meknes (Morocco): Optical Absorption and Raman Spectrometry

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Abstract: Samples of *zelliges*, from the Dar-El Beïda Palace built in Meknes (Morocco) in the 18th century, were studied by optical absorption and Raman spectroscopies. The results obtained by the two techniques were in agreement and show that the glazes of the zelliges are lead oxide–rich in composition. Other phases were also detected, mainly the SnO_2 cassiterite opacifier for the white glaze, and heamatite (α-Fe_2O_3) in association with magnetite Fe_3O_4 and manganese oxide (MnO_2) for the brown glaze. For the blue and green glazes, the elements responsible for the coloring are cobalt (Co^{2+}) and copper (Cu^{2+}), respectively.

Keywords: Chromophore ions, Dar-El Beïda Palace, glaze, optical absorption spectroscopy, Raman spectroscopy, *zellige*

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INTRODUCTION

The term *zelliges* indicates pieces of glazed ceramic carefully cut in geometric motifs and assembled to give traditional forms. The zellige is a part of the national cultural heritage that testifies of the technical, artistic, cultural, and economic knowledge of the man of the past. It was used for decoration in many ancient constructions such as palaces, mosques, medersas, and so forth. Unfortunately, its deterioration in the course of time led to its degradation (detachment of panels of zellige, detachment of glazes, etc.), and the ancient monuments lost a part of their value.

The restorations that were made until now were not satisfactory, because to identically re-create a piece of zellige, it is necessary to know exactly the characteristics of its components, in particular the colors. It is in this context that we have used physical techniques such as optical absorption and Raman spectroscopies that allowed us to identify the colors of zelliges and to determine the elements responsible for the coloring of the glazes. In this work, we describe and compare the results obtained by Raman and optical absorption spectroscopies from several samples of zelliges taken from Dar-El Beïda Palace (18th century; Meknes, Morocco).

MATERIALS AND METHODS

The samples of zelliges studied in this work were taken from Dar-El Beïda Palace situated in the southeast of the historical city (Medina) of Meknes. This palace was built between 1760 and 1775 under the administration of the Sultan Sidi Mohamed Ben Abdallah (Mohamed III).[1]

Three samples of zelliges of white (Mek814), brown (Mek818), and green (Mek824) colors were taken from one of the walls, and three others referenced by Mek831, Mek834 and Mek835 were taken from the grounds of the place reserved for women. All glazes are monochromatic and have thickness in the range 150–300 μm. The white, green, and blue glazes are characterized by the presence of partially unmelted quartz (their size can reach up to 100 μm). The bodies are very porous (the size of some pores is between 70 and 100 μm). The clay has a fine texture but contains several inclusions of varied sizes and colors. The bodies have a pink ochre color.

The Raman spectra were obtained using a Raman microspectrometer (JASCO Ventuno) with an Nd-YAG ion laser (532 nm). The power sent on the sample was approximately 30 mW. The optical absorption spectra measurements were made using a double-beam spectrophotometer (UV-Visible Pye Unicam Sp8-100d) in the spectral region from 300 to 800 nm.

RESULTS AND DISCUSSION

Optical Absorption Spectrometry

Figure 1 shows the optical absorption spectra of colors of different samples. All the spectra are characterized by the presence of two bands, one around 310 nm related to the intrinsic absorption characteristic of silicate glasses [2,3] and a broad shoulder located between 350 and 450 nm correlated with the absorption of light by the Fe^{3+} ions.[4,5] For the white glazes (Fig. 1a), no band was observed in the visible domain, and the presence of small concentration of iron would be responsible for the yellow shade of the glaze.[6]

The optical spectrum of the green glaze (Fig. 1b) shows a wide band between 550 and 800 nm correlated with the presence of Cu^{2+} ions in a glassy phase.[4] For the blue glaze, three bands were observed toward 536, 605, and 661 nm (Fig. 1c). These bands are characteristic of the allowed transitions of Co^{2+} ions in tetrahedral site.[3] The presence of Fe^{3+} ions, identified by the shoulder between 350 and 450 nm, allows the moderating of the blue color of the glaze.[7] In the case of the optical spectrum of brown glaze (Fig. 1d), we can distinguish a strong absorption in the entire visible

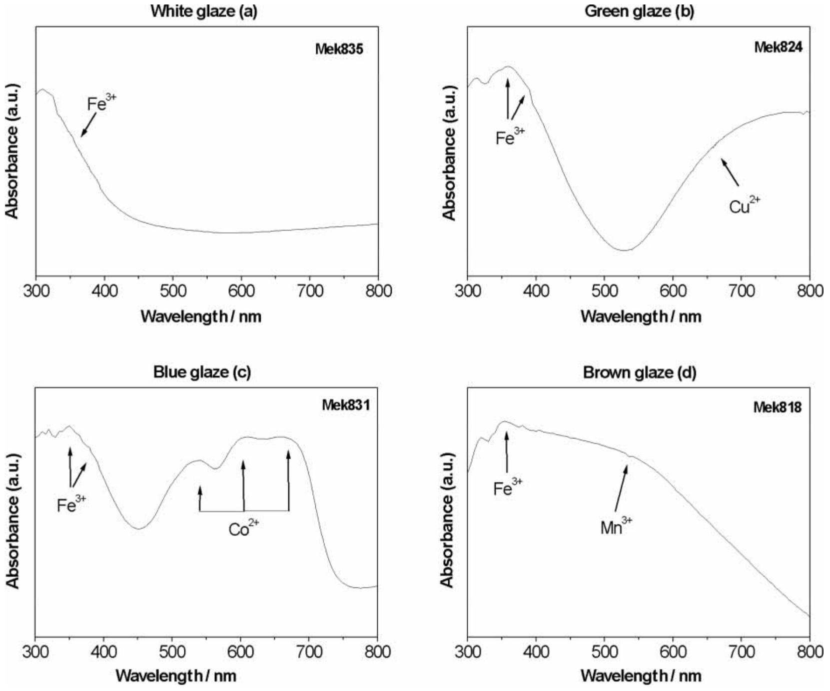

Figure 1. Optical absorption spectra in the visible domain of the glazes of Zelliges originating from Dar-El Beïda Palace. White (a), green (b), blue (c), and brown (d).

domain related to the presence of Mn^{3+} ions[8] and the bands characteristic of Fe^{3+} ions. Thus, the brown color is due to the combination of Fe^{3+} and Mn^{3+} ions.[9] The form under which the chromophore ions are present in these samples supposes the use of an oxidizing atmosphere during the firing. Besides, this study showed that the chromophore ions responsible for the color in these glazes are the same as those detected in glazes of zelliges of the 14th and 17th centuries. [10–12]

Raman Spectrometry

The Raman spectra of white, blue, green, and brown glazes are presented in Fig. 2. They show similar shapes composed of two very broad bands around 460 and 980 cm^{-1}. The first band is due to the bending vibration in the isolated SiO_4 (ν_2 mode).[13,14] The second corresponds with the Si-O bond stretching (ν_1 and ν_3 modes) in lead glaze.[15] The presence of the α-quartz phase is suspected in all glazes. The Raman spectra on some zones present only the α-quartz signature. Figure 3 shows one obtained for the brown glaze Mek818. This can be explained by the presence of partially unmelted quartz in the glaze.

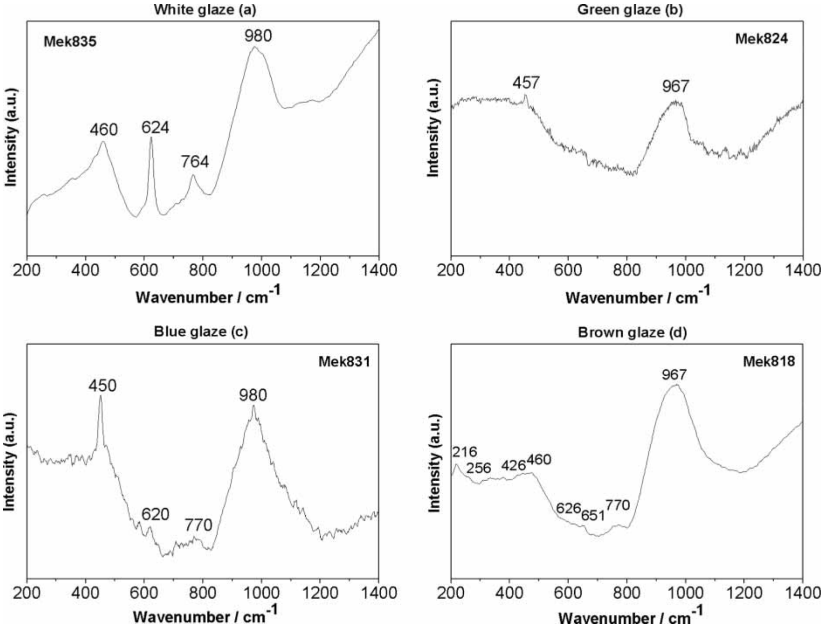

Figure 2. Raman spectra of the glazes of Zelliges originating from Dar-El Beïda Palace. White (a), green (b), blue (c) and brown (d).

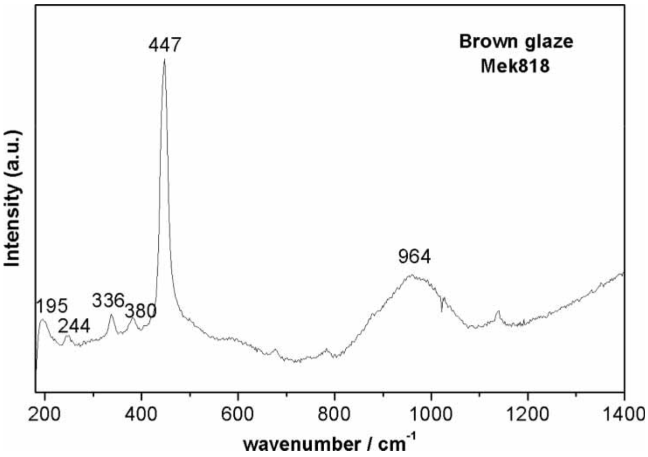

Figure 3. Raman spectrum recorded in the other zone of the brown Zellige. The spectrum is identical to that of α-quartz.

The coloring phases present in the glazes were also identified by Raman spectrometry. Thus, for the white glazes (Fig. 2a), we observed the presence of the Raman signature of the cassiterite (SnO_2), whose principal doublet is located around 621 cm^{-1} (strong) and 762 cm^{-1} (weak).[16,17] Having a high refracting index, it is used to mask the color of ceramic support and to give a white sight to glazes. We note that the cassiterite peaks were also detected in the green and blue glazes (Figs. 2b and 2c).

According to the results of the optical spectrometry, the green and blue colorings are due to the presence respectively of Cu^{2+} and Co^{2+} ions. However, Raman spectrometry did not detect any of these two elements. It is due, in the case of the green color, to the dissolution of Cu in a Pb-based glassy matrix. In the case of the blue color, the main peaks of cobalt oxide in lead glaze generally appear between 820 and 880 cm^{-1} for Co_2SiO_4, and for cobalt aluminate ($CoAlO_4$) they are located at 208 and 525 cm^{-1}.[16,18] These peaks do not appear clearly on the spectrum of Fig. 2c, probably because of the low content of cobalt oxide in this glaze. They can also be masked by the fluorescence or by the strong peak of quartz. Thus, the blue color of the glaze is due probably to Co^{2+} ions dissolved in the vitreous matrix.

The Raman spectra of the brown glaze (Fig. 2d) show the band at 216 cm^{-1} and the large band from 260 to 400 cm^{-1} characteristic of heated heamatite (α-Fe_2O_3),[19] and the low bands at 626 and 651 cm^{-1} attributed to traces of manganese and magnetite phase Fe_3O_4, respectively.[19,20] This result is in agreement with that of the optical absorption above, which revealed that the brown color of the glaze Mek818 is brought by the simultaneous presence of the Fe^{3+} and Mn^{3+} ions.

CONCLUSIONS

Raman and optical absorption spectrometries gave us important information on the color of zelliges, and they can be considered as efficient techniques for this genre of studies.

Raman spectrometry analysis showed the presence of the phase α-quartz (SiO_2) with a lead behavior in all the glazes and allowed identification of the phases responsible for their coloring: It is the cassiterite (SnO_2) for the white glaze, and hematite associated with the traces of magnetite (Fe_3O_4) and manganese oxide (MnO_2) for the brown glaze. For the blue and green zelliges, Raman spectrometry did not allow us to identify the responsible phases for the color of glazes generally because of the phenomenon of fluorescence or because the Cu^{2+} and Co^{2+} ions are probably dissolved in the vitreous matrix. The optical absorption spectrometry led to identification of the chromophore agents responsible for the colors: It is the Co^{2+} ions for the blue, Cu^{2+} ions for the green, and Fe^{3+} associated with Mn^{3+} ions for the brown.

The results obtained by both of these techniques are complementary and in agreement; they will certainly be very useful for re-creating missing parts of zelliges and thus for the restoration of historical monuments.

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