APPLICATION OF RAMAN AND FT-IR SPECTROSCOPY TO THE STUDY OF CERAMIC GLAZES

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ABSTRACT

Raman spectroscopy is a complementary technique to FT-IR spectroscopy, which is in widespread use. In this study both Raman and FT-IR spectroscopy are used to examine the structure of glazes customarily used in the ceramic sector, in which the base compositions have been varied by means of oxide additions such as Al_2O_3, BaO, K_2O, ZnO and CaO. The results obtained show that Raman spectroscopy generates much simpler spectra with narrow bands, while FT-IR spectroscopy produces very wide bands that usually overlap. This result, in addition to those commented at the beginning, makes Raman spectroscopy a very useful technique for the study and characterisation of ceramic glazes. Both spectroscopies have been used to obtain structural group Q^n (n=1, 2, 3 and 4) concentrations in the glazes, as well as their variation as a function of their chemical composition. In particular, Raman spectroscopy generates absorption peaks at 1045, 1011 and 903 cm^{-1} associated with groups Q^3, Q^2 and Q^1, which demonstrates the depolymerisation of the glassy structure of SiO_2 caused by the incorporation of modifier oxides.

1. INTRODUCTION

In the recent years, Raman spectroscopy has acquired a fundamental importance in the characterisation of any type of material, which is due to its great versatility, since it is a non-destructive, fast technique, and the availability of increasingly economic instruments. Nowadays, it is possible to find even low-priced portable instruments whose results are comparable to more specific instruments. On the other hand, this spectroscopy is complementary to the widely used infrared spectroscopy (FT-IR) and between both they can contribute important information on the glassy structure. Nowadays, many studies conducted with Raman spectroscopy allow determination of the content of different silica structural groups, commonly known as Q^n in which n indicates the number of oxygens that are united to silica atoms. In the present study, the different results are shown that can be obtained with the two mentioned spectroscopies and how they serve to achieve greater knowledge of the glassy structure in frits and ceramic glazes[1].

2. EXPERIMENTAL

The glazes analysed by Raman and FT-IR spectroscopy were prepared from frits of the same composition using an industrial firing cycle. In a reference frit of composition: 55% SiO_2, 5% Al_2O_3, 20% CaO, 3% BaO, 10% MgO, 7% K_2O the composition was modified, varying the Ba concentration in regard to Si, Al, K and Mg in percentages between 0 and 15%. These frits were used to prepare glazes with no type of additive, so that only the firing process would influence the glassy structure of both the frit and the glaze. The frits and the glazes were referenced Ba-Si, Ba-Al, Ba-K and Ba-Mg, adding an **f** or an **e** at the beginning to indicate whether it was a frit or glaze, respectively. The FT-IR spectra were conducted on powder samples diluted in KBr. A Perkin-Elmer 1760 X IR spectrophotometer was used, in the medium infrared, with a resolution of 2 cm^{-1}. On the other hand, the Raman spectra were also obtained with the powder samples using a Renishaw inVia instrument with Leica camera and laser of 514.5 nm, power of 25 mW. In this case the effect of the power of the laser, as well as the incident focus, was previously studied.

3. RESULTS

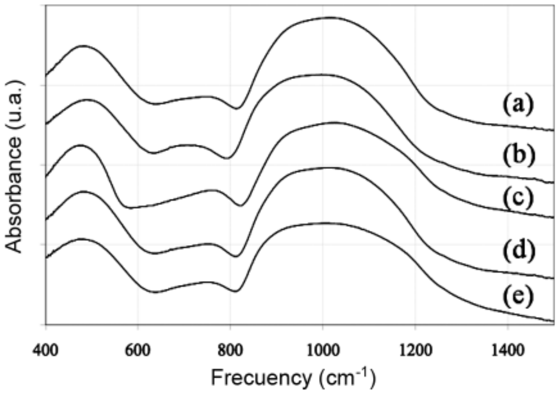

Figure 1. FT-IR spectra of frits.
(a) f-3Ba10Mg, (b) f-15Ba45Si;
(c) f-15Ba0Mg; (d) f-8Ba0Al; (e) f-7Ba3K

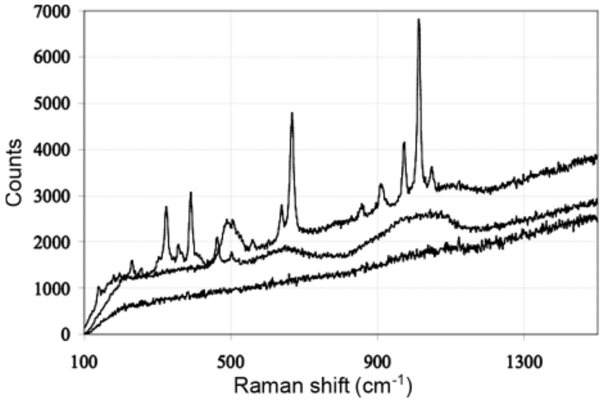

Figure 2. Raman spectra of frits and glazes.
(a) f-0Ba10K-10%; (b) f-0Ba10K-100%;
(c) e-0Ba10K-100%

Figure 1 displays the FT-IR spectra of different frits. The spectra for the glazes were practically the same and for that reason they are not shown here. It may be observed that all are quite similar, independently of the concentration of the modifier elements in the glassy network. In these modifier elements, the wide band at 1020 cm^{-1} (asymmetric stretch vibration), as well as the two small 740 ones (symmetrical stretch vibration), and 480 cm^{-1} (bending vibration) correspond to Si-O-Si bonds. The displacement of these bands in regard to those of silica (1080, 800 and 460 cm^{-1}) is due to the presence of network modifiers[2].

On the other hand, Figure 2 shows the Raman spectra for the same frit and its glaze. The percentage values in the reference of each spectrum indicate the power used with the laser. In this case, unlike the IR spectroscopy, the glazes display much narrower bands than those of the corresponding frits, which is due to crystallisations in the glaze. These differences are not noted in the FT-IR spectra. This result of the Raman spectroscopy indicates the great usefulness of this technique when it comes to characterising glazes, it being much faster than X-ray diffraction.

Leaving aside this advantage of Raman spectroscopy, the spectra corresponding to the frits are quite similar to those obtained by FT-IR, though the Raman spectra show only two areas. This fact, together with the fact that it is possible to deconvolute them in the two areas (500-800 or depolymerisation area, and 800-1300 or polymerisation area), allows the glassy structure of the frit to be determined[3]. In addition, analysis of the area ratio of both areas enables the polymerisation index (IP) to be determined of the glassy network[3]. In this study we have performed these analyses and the bands obtained are at 870, 935, 990, 1072 and 1160 cm^{-1}, which may be assigned to groups Q^0, Q^1, Q^2, Q^3 and Q^4, respectively, i.e. $Si(O)_4^{4-}$, $Si(O)_4^{3-}$, $Si(O)_4^{2-}$, $Si(O)_4^{1-}$ and SiO_4. The analysis of the evolution of each of these bands has shown that the substitution of certain modifier elements by others causes the relation between the different bands and therefore between the different structural groups to vary. It has been observed that the bands that display more variation are located at 1072 and 990 cm^{-1}. Figure 3 shows the evolution of these bands. It shows that the substitution of Ba for Si causes a decrease in the number of Si groups joined to three O bridge atoms, a fact that also occurs when Mg or Al substitute Ba. However, it may be observed that if K substitutes Ba, the concentration of these groups increases up to K values of 8%, decreasing at larger percentages.

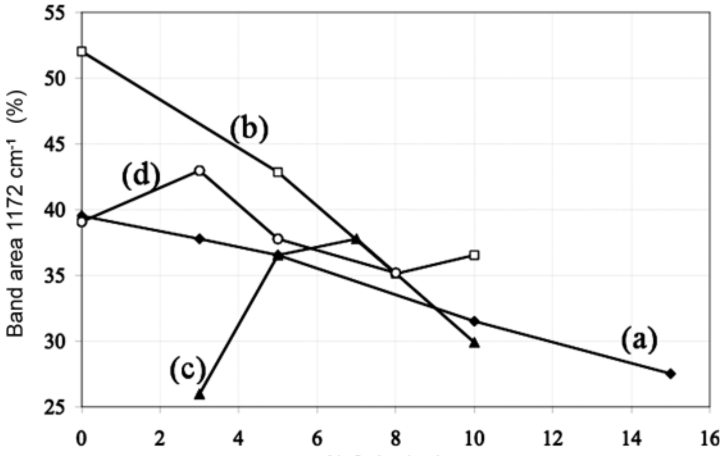

Figure 3. %$Si(O)_4^{1-}$ groups when substituting: (a) Ba for Si; (b) Mg for Ba; (c) K for Ba; (d) Al for Ba

4. CONCLUSIONS

In this work it has been shown that Raman spectroscopy is very useful when it comes to characterising frits and glazes, particularly in regard to their structure. The results obtained for the glazes make important applications of this technique foreseeable in the field of ceramic floor and wall tiles.

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