STRUCTURAL STUDY OF CERAMIC GLAZES BY FT-RAMAN SPECTROSCOPY

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1. INTRODUCTION

As ceramic frits and glazes have evolved to yield ceramic glazes with improved technical and aesthetic performance, the number and type of instrumental techniques used to study and characterise these ceramic glazes have also increased. Thus, nowadays it is common to find XRF, XRD, electron microscopy instruments, etc. not just in research centres or universities, but also at ceramic companies.

In this sense, a widely used technique in the scientific field for the information it supplies regarding the structure of a great variety of materials (polymers, glasses, etc.), whose potential application for the study of ceramic glazes, however, has not yet been evaluated, is Fourier-transform Raman spectroscopy (polarised FT-Raman). A vibrational technique is involved, which, like infrared spectroscopy, is based on the inelastic scattering of light that impinges upon a material as a function of the polarisability of the molecules or ions contained in this material. When a beam of infrared light strikes the surface of a solid sample, the material absorbs this radiation, emitting two different types of scattering. Most of the scattered photons are elastically emitted, i.e. that they keep the wavelength, forming what is known as the Rayleigh scattering. However, a small number of the scattered photons are inelastically emitted and change wavelength, forming what is known as the Raman scattering, since it was the physicist C.V. Raman who identified this photon scattering, work for which he received the Nobel Prize for physics in 1930. However, Raman spectroscopy has had to wait until the 1960s, the decade in which lasers were invented, for it to be used systematically in research laboratories, since the intensity of the inelastically scattered light is very low, which is why high incident energy irradiances on the sample are required, such as those provided by laser systems. Little by little this technique has found its place between the different spectroscopic techniques and nowadays it contributes information on sample composition and on other characteristics, such as the degree of crystallinity, crystal size and orientation, stresses or isotopic composition. Furthermore, it allows observing electronic and magnetic excitations in certain materials, which provides more information on these and, in addition, also enables characterising all types of materials in any state (gas, solid or liquid).

Raman spectroscopy is increasingly being used in research centres and companies. This is because the instruments have evolved satisfactorily in regard to size, versatility and price. At present, numerous companies use this type of spectroscopy to monitor chemical processes in real time, to control production process quality, to control and determine gas composition, etc.

In the particular case of materials with silicon-based glassy phases, this technique enables, among other things, to distinguish structural differences in the silicate network as a function of the type and concentration of the modifying oxides. Ceramic glazes can be considered a type of such materials, since they are glazes with structural networks of the silicate, aluminosilicate or boroaluminosilicate type in which the SiO_4 tetrahedrons are linked by oxygen atoms located at the corners. These interconnections between tetrahedrons are modified when zirconium, zinc, etc. are incorporated, especially with alkaline or alkaline-earth elements. Most of these atoms, particularly the last ones, produce a break in the silicate glassy network, giving rise to depolymerisation; for this reason they are called network modifiers. The depolymerisation equilibrium of a tetrahedral SiO_4 network that was completely polymerised can be expressed by the following equation:

$$\text{O-Si-O-Si} + M_{2/\nu}{}^{\nu+} \Leftrightarrow 2\text{SiO}^{-} + 2/\nu M^{\nu+} \qquad [1]$$

where M is the modifying cation of charge $\nu+$

Since the SiO_4 tetrahedrons, polymerised or not, display Raman bands, it is possible to use this technique to analyse such modifications by the vibration modes of these units and their combinations. For this, it is necessary to analyse the spectra, assigning an intensity, mean width and spectral position to each of the bands appearing in the spectra.

In accordance with equation [1] the degree of depolymerisation essentially depends on the network-modifying ion concentration. However, it is known that in glasses, these modifiers tend to be grouped in zones, causing so-called phase separation[3]. At the same concentration of a given cation, this phase separation basically depends on the type of cation (size, charge, etc.) and on the composition and concentration of the network-forming ions. In any case, the depolymerisation reaction shown in equation [1] unfolds with the rupture of the bonds in which bridge oxygens participate. In this sense, it is common to assume the presence of different structural units in silicate glasses. These units are expressed by means of the quaternary designation Q^4, Q^3, Q^2, Q^1 and Q^0 in which Q indicates the SiO_4 tetrahedron and the superscript the number of its bridge oxygens. Thus, Q^0 would correspond to the SiO_4 monomer, i.e. to isolated silica tetrahedrons, whereas Q^4 would correspond to a completely polymerised network with all the Si atoms linked by O atoms, without leaving any free bond. According to the literature the Q^4, Q^3, Q^2, Q^1 and Q^0 units originate Raman bands at different frequencies. McKeown has assigned the band that appears at 1075 cm^{-1} to the first two groups, the band at 975 cm^{-1} to Q^2, and those at 930 and 885 cm^{-1} to groups Q^1 and Q^0, respectively. However, Colomban has assigned the bands located at 1250-1150 cm^{-1}, 1100 cm^{-1}, 1100-1050 cm^{-1}, 950 cm^{-1} and 850-800 cm^{-1} to the 5 groups mentioned, respectively, according to the increase in the number of non-bridge oxygens[5,6].

Although all these bands appear in the 1200-800 cm^{-1} region, i.e. in which the Si-O bond stresses occur, it is also very interesting to analyse the 600-200 cm^{-1} region, corresponding to the bending vibrations of these bonds, since these provide information on the degree of polymerisation of the glassy network (6,7).

2. OBJECTIVE

The present study seeks to evaluate the usefulness of FT-Raman spectroscopy for analysing ceramic glazes from a structural point of view. For this, the variation of the Q^n units and the polymerisation of the glassy lattice of different ceramic glazes as a function of zirconium silicate and aluminium oxide content have been studied. These data can be of great use in correlating the properties of ceramic glazes with glaze glassy structure.

3. EXPERIMENTAL

3.1. MATERIALS

For the analysis of glazes with different zirconium silicate contents, frits with increasing zirconium oxide contents were used, as set out in Table 1. These frits were used to prepare the corresponding glazes, adding kaolin and additives in the proportions typically used in the ceramic sector.

Table 2 details the compositions of the glazes used in the study of the variation of Q^n units as a function of the aluminium oxide addition. The C0 frit in Table 1 was used as the base frit, and contained no zirconium oxide.

In each case, the glazes obtained after milling their components with water were applied onto engobed porous single-fire ceramic bodies and subjected to a conventional firing cycle with a peak temperature of 1110 ºC.

OXIDE	FRITS				
	C0	C2.5	C5	C10	C15
SiO_2	59.3	57.9	56.3	53.3	50.5
Al_2O_3	4.9	4.7	4.6	4.4	4.1
B_2O_3	5.5	5.4	5.2	5.0	4.7
RO (R=Ca, Mg)	11.2	10.9	10.7	10.1	9.5
ZnO	13.9	13.5	13.2	12.5	11.8
R_2O (R= Na, K)	5.2	5.1	5.0	4.7	4.4
ZrO_2	0.0	2.5	5.0	10.0	15.0
TOTAL	100.0	100.0	100.0	100.0	100.0

Table 1. Frit compositions expressed in % by weight of oxides, with increasing zirconium oxide contents.

COMPONENT	GLAZES							
	A0	A1	A2	A3	A5.0	A7.5	A10	A15
Frit C0	100.0	99.0	98.0	97.0	95.0	92.5	90.0	85.0
Al_2O_3	0.0	1.0	2.0	3.0	5.0	7.5	10.0	15.0
Kaolin	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Additives	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 2. Glaze compositions expressed in % by weight of each component, with increasing alumina additions.

3.2. TECHNIQUES

The glazes of the pieces obtained according to the procedure indicated in the previous section were studied by XRD and FT-Raman spectroscopy. Neither technique required special preparation of the sample, so that the original piece was simply cut into samples of the appropriate size for analysis.

XRD analysis was performed with a Philips PW1820 instrument with Cu W2200 KV60 tube. Scanning was carried out from $^{\circ}2\theta = 4$ to $^{\circ}2\theta = 40$, at a rate of 0.055 $^{\circ}2\theta/s$, voltage of 40kV and amperage of 30mA.

For the Raman analyses a micro-Raman RM2000 instrument was used, fitted with a Leica microscope to focus the sample and select the zone whose spectrum was to be obtained. A magnifying lens of 100x was used, which produced a spot (incident laser diameter) of 10 μm. The excitation source was line 514.5 nm provided by an Ar^+ laser. The laser output power was 40 mW, with incident radiation on the sample of 2.5 mW, which avoids any thermal effect on the samples. The analysed frequencies were between 1300 and 100 cm^{-1}. The exposure time for each spectrum was 10s, making 5 accumulations with which the final spectrum was obtained. The Raman spectra were analysed in both the conventional system and with polarised light, for which a polarising crystal placed between the sample and the Raman source, and an analysing crystal at the signal input to the spectrometer were used. Analysis by polarised light was made for polarisations of incident and scattered light keeping parallel orientations, i.e. VV (vertical/vertical). The calibration of the Raman spectrophotometer and of the polariser was made with metallic Si and CCl_4 respectively. In order to obtain a statistical plot of the results, measurements were made in different regions of each glaze.

3.3. METHODOLOGY: MATHEMATICAL TREATMENT OF THE SPECTRA

The Raman spectra obtained were treated mathematically by first performing a baseline correction (assuming this to be a polynomial of the type x^3 or x^4), followed by smoothing (Savinzki-Golay with a range of 9-points), and finally analysis of each spectrum by deconvolution. The deconvolution process was also conducted using an own software, which assumes the spectrum is made up of Gauss-type bands, each of which is defined by three parameters: intensity, mean width and position. Generally, both intensity and position can be obtained from data in the literature, although in our case an analysis was performed of the second derivative of each spectrum, which enables assigning each of these three parameters to the bands existing in the spectrum. With all these data and their respective analysis each Raman spectrum was deconvoluted, obtaining the bands of best fit. The area of each band was calculated in order to perform a semi-quantitative analysis of each spectrum. To obtain the greatest possible precision by the deconvolución process, this was carried out by spectral zones, choosing two as the most important zones: the one between 1200 and 800 cm^{-1} and the one between 700 and 100 cm^{-1}.

4. RESULTS

4.1. EFFECT OF BEAM POLARISATION IN THE SIGNAL OBTAINED BY RAMAN SPECTROSCOPY

As the Raman signals in both glassy silica and glasses are highly polarised[8] and no references are available for ceramic glazes, the first aspect studied was the effect of beam polarisation on the signal obtained. The Raman spectra were made, therefore, both in the normal and polarised mode (V/V) of two ceramic glazes obtained from glazes which contained, in one case the C0 frit indicated in Table 1 with the usual additives (kaolin, deflocculants, etc.) and, in the other case, the same composition with an addition of 15% zirconium silicate with a particle size below 5μm as glaze raw material.

The results obtained are shown in Figure 1, which shows that for the glaze containing no zirconium silicate the non-polarised Raman spectrum (C0) is practically flat, displaying a wide band at 1100 cm^{-1} attributed to the Si-O-Si bonds[7] However, the polarised Raman spectrum (C0-pz) exhibits two wide and one very small band located at 1020, 470 and 800 cm^{-1}, respectively, bands which are also assigned to Si-O-Si bond vibration modes[7]. On the other hand, the Raman spectra of the glazes that contain zirconium silicate (C15 and C15-pz) display very intense peaks, the most important of which are located at 1006, 975, 438, 356, 270, 210 and 200 cm^{-1} and are attributed to Si-O-Zr bonds[9] of this compound. In this case the bands corresponding to the Si-O-Si bonds are not observed due to the high intensity of the Si-O-Zr bond bands, although when the polarised spectrum is expanded, these bands appear with a similar intensity to that of the C0-pz spectrum bands. In view of these results it was decided to perform all the spectra with polarised light.

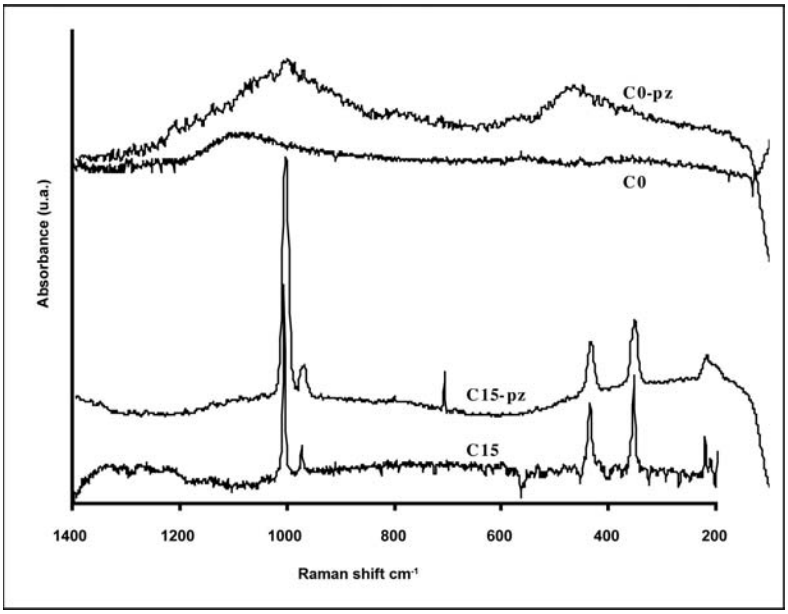

Figure 1. Non-polarised and polarised (pz) Raman spectra of ceramic glazes. C0 ⇒ without zirconium silicate. C15 ⇒ with 15% zirconium silicate

4.2. EVOLUTION OF THE GLAZE STRUCTURE AS A FUNCTION OF THE ZIRCONIUM OXIDE CONTENT IN THE FRITS

The glazes made with the frit compositions indicated in Table 1 were analysed first by XRD to determine the degree of zirconium silicate devitrification. The resulting signal was observed to increase as the zirconium silicate content in the frit increased, and crystals were even detected in the sample that contained 2.5% zirconium oxide in the frit.

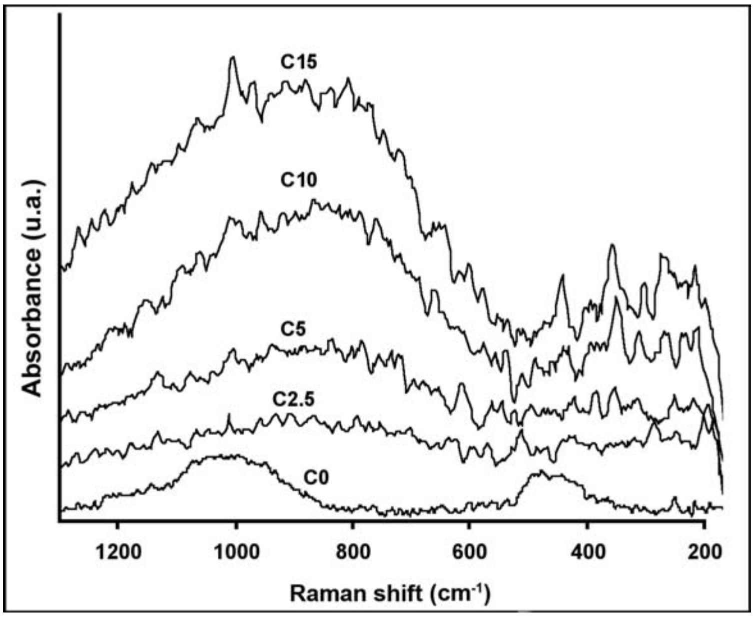

Figure 2. Polarised Raman spectra of ceramic glazes obtained from frits with different zirconium oxide contents (0 to 15%).

Figure 2 shows the Raman spectra obtained for the glazes in which the zirconium silicate devitrifies from the frits listed in Table 1. It shows that the zirconium silicate peaks (band located at 1005 cm^{-1}) are less intense than those produced by this compound when it is added to the glaze composition as a raw material. This result is due to the different zirconium silicate crystal sizes and distribution in glaze[10]. As Figure 2 shows, the bands of the glassy phase are as intense as those of the devitrified zirconium silicate, those of the latter practically being included in those of the former.

Analysis of these spectra by deconvolución yielded the evolution of the existing bands, each of which was assigned to the different groups, as previously described. Thus, in the spectral region 1300-800 cm^{-1} the C0 sample displays 5 bands at 1185, 1093, 1015, 945 and 880 cm^{-1}, originated by the different structural groups of silica existing in the glaze. Based on their position these bands are assignable to groups Q^4, Q^3, Q^2, Q^1 and Q^0 respectively. As the zirconium oxide content in the frit is increased a new band appears around 1006 cm^{-1}, and at high contents another one also appears around 975 cm^{-1}; these are bands that correspond to zirconium silicate that has devitrified in the glaze during firing.

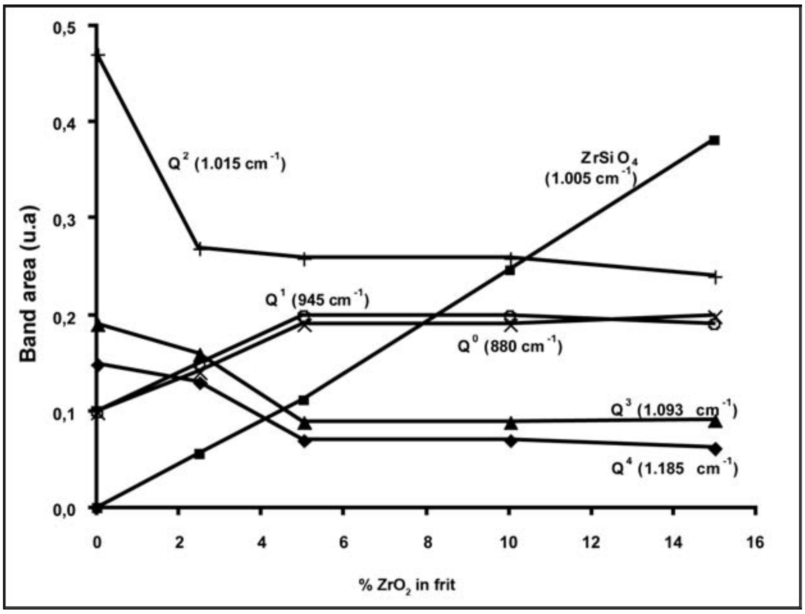

Figure 3. Evolution of the bands corresponding to Q^n units and of the zirconium silicate band in ceramic glazes obtained from frits with different zirconium oxide contents.

The evolution of these bands, shown in Figure 3, points to several facts which need to be taken into account. The most important is that structural groups Q^4, Q^3 and Q^2 diminish and Q^1 and Q^0 increase as frit zirconium oxide content is raised. This evolution is very significant up to zirconium oxide contents of 5%, beyond which the variation of the Q^n units is much smaller. These results indicate that the glassy network is being broken up as the devitrified zirconium silicate percentage increases, leading to a rise in the number of non-bridge oxygens, since only the Q^1 and Q^0 groups grow, allowing the following reactions to be considered:

$Q^4 \rightarrow Q^3 + Q^1$
$Q^3 \rightarrow Q^2 + Q^1$
$Q^2 \rightarrow 2Q^1$
$Q^2 \rightarrow Q^1 + Q^0$

A similar result has been demonstrated by other researchers, who observed the break-up of the glassy lattice during fusion glass when ZrO_2 was added[5].

With regard to the polymerisation of the glassy network, Figure 4 depicts the evolution of the different bands in the region 660 – 200 cm^{-1} as a function of the frit zirconium oxide content. It shows that raising zirconium oxide decreases three-dimensional polymerisation (band at 444 cm^{-1}) and linear polymerisation (band at 495 cm^{-1}), which indicates that the network-modifying elements are distributed more homogenously in the glassy matrix. The band assigned to 3-member rings remains practically constant.

Finally, it is important to note that the characteristic zirconium silicate bands that appear at 1006 cm^{-1} and at 358 cm^{-1} increase linearly as the frit zirconium oxide content is raised, as Figures 4 and 5, respectively, show. The fit of the areas of these bands as a function of frit zirconium oxide content provides straight lines with very similar slopes and coefficients of regression, 0.025 and 0.998, respectively, for the 1006 cm^{-1} band and 0.022 and 0.997 for the 358 cm^{-1} band. These experimental data corroborate one of the advantages that Raman spectroscopy affords, namely that the crystalline compounds tend to show few peaks, which have a small mean width, moreover, so that they do not overlap. The data also indicate that the signal obtained with this technique is directly proportional to the concentration of the active species, provided source intensity is the same. All these features suggest it is an appropriate technique for quantitation of the devitrified zirconium silicate content in ceramic glazes.

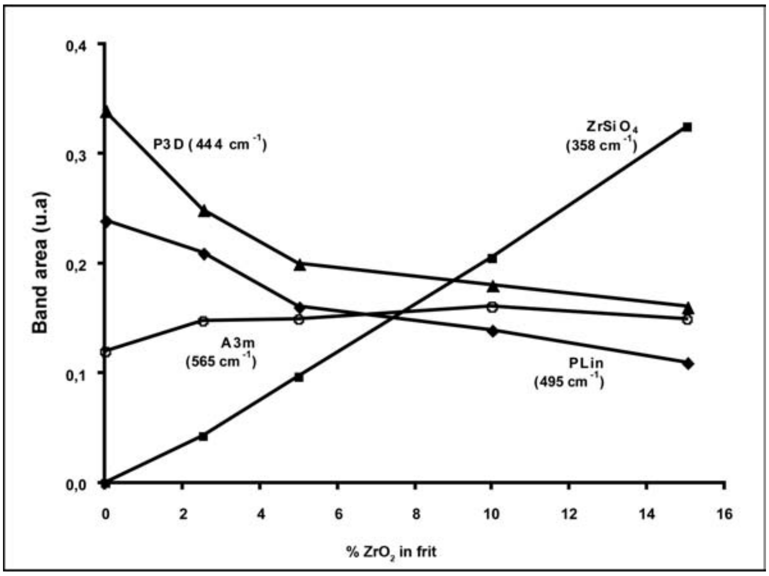

Figure 4. Evolution of the bands corresponding to polymerisation of the glassy lattice in ceramic glazes obtained from frits with different zirconium oxide contents (P3D: three-dimensional polymerisation/ PLin: linear polymerisation / A3m: three-member rings).

4.3. EVOLUTION OF GLAZE GLASSY STRUCTURE AS A FUNCTION OF THE ALUMINIUM OXIDE ADDITION TO THE GLAZE.

As in the previous case, the glaze coatings obtained with the glaze compositions indicated in Table 2 were analysed by XRD. The resulting diffractograms (Figure 5) show that the signal corresponding to the residual alumina not incorporated in the glassy matrix begins to appear slightly in sample A3 (3% alumina addition), though it is not until the 7.5% addition that the peaks begin to appear more clearly, which suggests an excess of alumina that is no longer digested by the glassy phase.

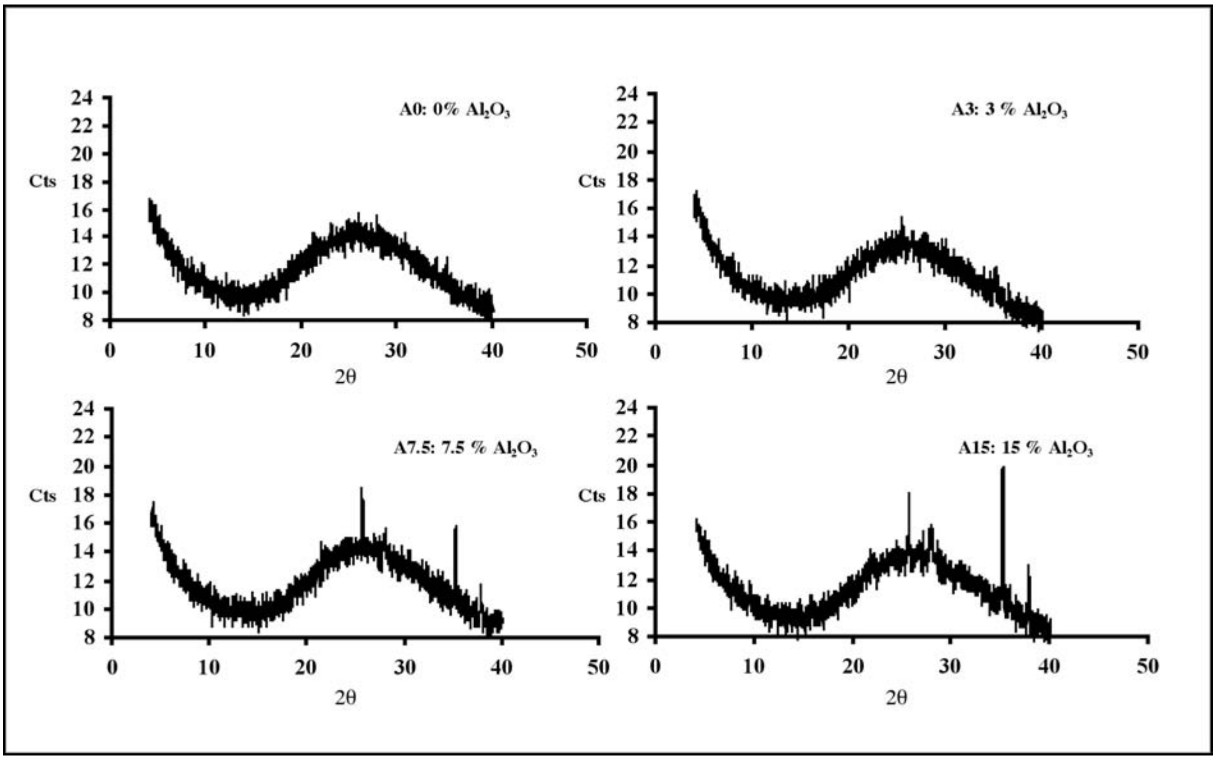

Figure 5. XRD of ceramic glazes with different alumina contents.

Figure 6 depicts the FT-Raman spectra of the glazes obtained from glaze compositions detailed in Table 2, which evidence slight changes in the spectral region in which the variation of Q^n units is evaluated, and somewhat more pronounced changes in the region in which silica polymerisation is analysed. The analysis by deconvolución of these two regions is presented in Figures 7 and 8.

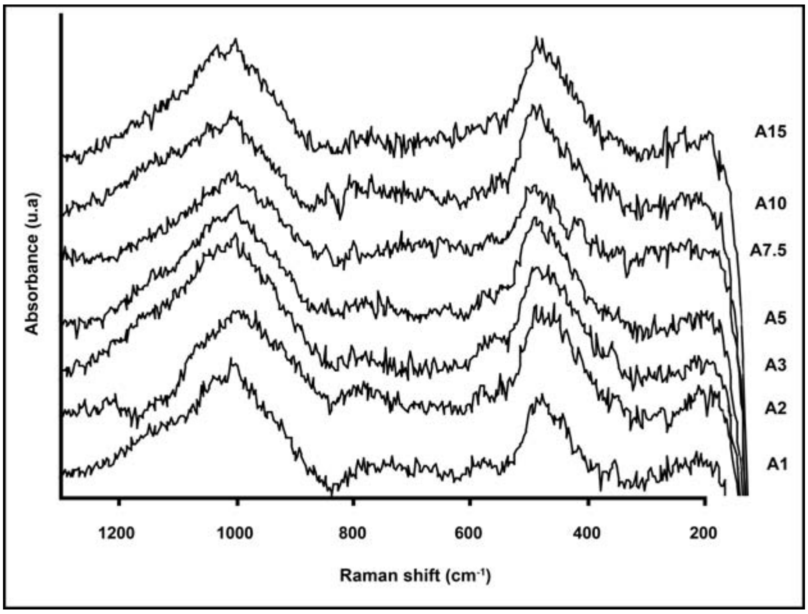

Figure 6. Polarised FT-Raman spectra of ceramic glazes with different alumna contents (1 to 15 %)

Figure 7 shows that the evolution of the bands corresponding to Q^n units can be described according to the following reactions:

$Q^4 \rightarrow Q^3 + Q^1$
$2Q^2 \rightarrow Q^3$

since a reduction in the Q^4 and Q^2 groups, principally the Q^2 groups, and an increase in the Q^1 and Q^3 groups can be observed. This finding suggests that the glassy network becomes stronger because the number of non-bridge oxygens decreases.

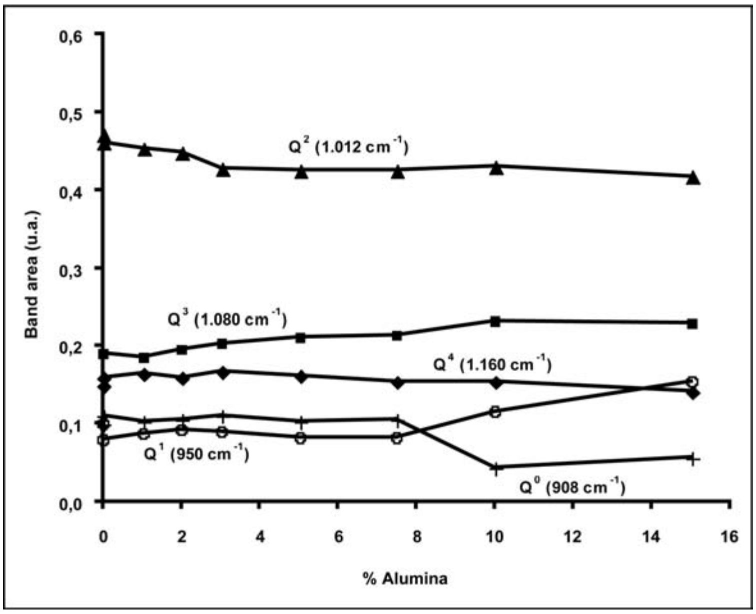

Figure 7. Evolution of the bands corresponding to Q^n units in ceramic glazes with different alumina contents.

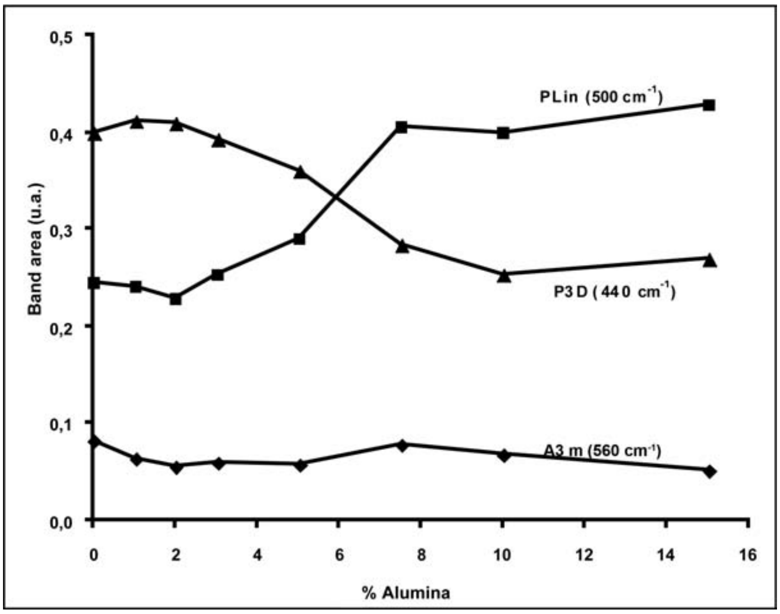

Figure 8. Evolution of the bands corresponding to polymerisation of the glassy lattice in ceramic glazes obtained from frits with different alumina contents (P3D: three-dimensional polymerisation/ PLin: linear polymerisation / A3m: three-member rings).

In regard to the spectral region corresponding to the polymerisation of the glassy network (Figure 8), when the alumina content is raised the three-dimensional polymerisation (444 cm^{-1}) initially grows very slightly up to 2-3 % additions of Al_2O_3 and then decreases up to 7.5% additions of Al_2O_3, finally stabilising at larger percentages. This result indicates that at low alumina contents (<3%), the alumina enters and becomes part of the glassy structure, acting as a network former, whereas at greater contents, the alumina no longer forms glassy network and contributes to distributing the modifying elements more homogenously throughout the glassy structure, thus diminishing the three-dimensional polymerisation. This result is consistent with the XRD observations, since it is above 3% additions when residual alumina begins to be detected, although it is not until contents of 7.5% that the peaks are clearly defined.

As far as linear polymerisation (495 cm^{-1}) is concerned, this is observed to display an opposite evolution to three-dimensional polymerisation, i.e. it increases for additions between 3 and 7.5%, stabilising at larger values, which again agrees with the XRD data.

Finally, note that the band attributed to the ring of three silica members hardly changes with the alumina concentration, just as occurred in the glazes obtained from frits with different zirconium silicate contents.

5. CONCLUSIONS

The foregoing discussion allows drawing the following conclusions:

1. The usefulness of FT-Raman spectroscopy for the study of ceramic glaze structure has been demonstrated. It enables monitoring the evolution of the different structural units, analysing the furthest ranging groupings or polymerisation of the network, and monitoring devitrified crystal formation in the firing.
2. It is necessary to use the polarised mode in realising the spectra, since the Raman signals obtained of the ceramic glazes are highly polarised, just as occurs with glassy silica or types of glasses. This enables obtaining clear bands that they can be assigned to the vibration modes of Si-O-Si, Si-O-Zr, etc.
3. In ceramic glazes with different zirconium silicate contents, bands corresponding to the Q^n (n= 0 a 4) units and two bands characteristic of zirconium silicate have been identified in the spectral region between 1300 and 800 cm^{-1}, whereas in the region 660–200 cm^{-1} bands due to the polymerisation of the glassy network and another band, again due to zirconium silicate, are observed:
    - The structural groups Q4, Q3 and Q2 diminish, whereas groups Q1 and Q0 increase as the amount of devitrified zirconium silicate in the glaze increases; this variation is very significant up to zirconium oxide contents in the frit of 5%. These variations indicate the break-up of the glassy network and creation of non-bridge oxygens.
    - The increase in zirconium silicate diminishes the three-dimensional and linear polymerisation, which indicates that the network-modifying elements are distributed more homogenously in the glassy matrix.
    - The characteristic zirconium silicate bands increase linearly as the zirconium silicate in the glaze is raised, which indicates the possibility of using this

technique to quantify the amount of zirconium silicate that devitrifies in ceramic glazes.

4. In ceramic glazes with different alumina contents the bands corresponding to the Q^n (n= 0 a 4) units in the spectral region between 1300 and 800 cm^{-1} have been identified, as have the bands relating to the polymerisation of the glassy network in the region 660-200 cm^{-1}:

   – The variation of the Q^n units is less pronounced than in the case of glazes with different zirconium silicate contents, and displays a decrease in the Q^4 and Q^2 groups and an increase in the Q^3 and Q^1 groups, which involves a reduction in the number of non-bridge oxygens.

   – The linear and three-dimensional polymerisation remains practically steady at alumina contents below 3%, without any residual alumina peaks being detected either by XRD, which indicates that the aluminium enters and forms part of the glassy network, acting as a network former and generating large regions in which there are few modifying elements.

   – For alumina contents between 3 and 7.5 %, three-dimensional polymerisation decreases rapidly, whereas linear polymerisation grows in the same measure, with XRD detection of very weak residual alumina peaks. This all indicates that alumina no longer forms part of the glassy network and contributes to a more homogenous distribution of the modifying elements throughout all the glassy structure.

   – When the alumina content exceeds 7.5%, both the three-dimensional and linear polymerisation remains steady and a clear residual alumina signal is detected by XRD.

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