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Phase changes of ceramic whiteware slip-casting bodies studied by XRD and FTIR

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Abstract

The phases of white ceramic test bodies conformed by wet processing route, that are formed during firing were studied and characterized by X-ray diffraction and FTIR spectroscopy. The materials were prepared by slip-casting, then conveniently dried, and submitted to a programmed firing process. The phases developed in each stage of the thermal treatment were controlled by X-ray data. The IR vibrational spectra of the samples were recorded and discussed based on the crystal chemistry of the phases present. The sequence of phase transformation was also analyzed using both techniques. These methods allow to record the modal (true) compositions of the materials with adequate accuracy and also to correlate them with the chemical composition.

Keywords: White ceramics; XRD phase development; IR spectra

1. Introduction

Ceramic whiteware manufacture is a system of such complexity that it offers renewed opportunities for research despite the plethora of published works in this area [1]. The complex interplay between raw materials, processing routes, microstructure and mechanical properties poses the necessity to develop the basic knowledge from the perspective of the science of materials to face major challenges such as new products and improved automatization processes.

Kaolin, feldspar and quartz are used as raw materials in conventional porcelain production. If the raw material ratios are changed or if feldspar and quartz are replaced by some other materials, the characteristics of the prepared porcelains change. The firing properties vary depending on the types of the raw porcelain batch components and their particle size distribution.

Owing to the considerable amount of energy consumed in the conventional double firing process applied in porcelain production, which is one among other disadvantages, great importance has been given to single firing processes. This procedure is based on the formation of anorthite phase ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) instead of mullite ($3Al_2O_3{\cdot}2SiO_2$) formed after long firing [2].

The application of wet processing assures triaxial blends of the highest mixing homogeneity to obtain strength and integrity of the microstructure of the ceramic body. According to the wet processing route, the mixture of kaolin, ball clay and nonplastics, is to some extent, slurried together in tap water with different additives, as in slip [3]. This suspension is manufactured mainly for sanitary ware and also to produce small particles in a jet sprayer to obtain products related to many industries. The slip-casting method, much used in ceramic production, makes it possible to reproduce very complicated shapes in plaster moulds.

In the present integrative study, two categories of clay-based slurries, called ‘‘barbotina’’ (slip), which are commercially available for the local ceramic manufacturing industries, were applied to prepare the test samples by solid slip-casting forming. After drying and firing, following an established firing schedule, the ceramic bodies obtained at each stage were submitted to XRD and FTIR analysis in order to check the structural changes during the process. The advantage of using both techniques as complementary tools is discussed.

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Table 1
Firing schedule at highest temperature (P1200)

Time (min)	60	60	60	60	60	60	90	Total firing time: 7 h 30 min.
Temperature (°C)	150	300	500	700	950	1100	1200	

2. Experimental procedure

Test samples were prepared with commercial suspensions of similar granulometry labelled S when the material is applied to spray-drying processes and P for pottery and other general purposes. The main steps included: control of the stability of suspensions followed by the incorporation of the corresponding dispersant or deflocculant in order to obtain a stable quick-casting slip [3]. Once the suspension had the adequate balance in density and viscosity, bar samples of 2 cm × 4 cm × 0.5 cm of dimension were formed by solid casting. After the casting process in plaster moulds, the bodies were carefully air dried.

The heating of both kinds of test samples was carried out, simultaneously, in a furnace oven, in the open air, up to the maturation temperatures, and then allowed to cool inside the oven. Irreversible changes were measured by heating the specimen to a series of temperatures, then cooling and measuring.

Typical temperatures were selected in order to study the raw material behaviour during firing on the laboratory scale [4]. According to this schema the firing schedule, was carried out as shown in Table 1.

The ceramic bodies were conveniently crushed and then ball milled for a few minutes. The resulting powders were submitted to analysis by X-ray diffraction and FTIR vibrational spectroscopy. X-ray diffraction patterns were collected at 25 °C, using an automated PW model 3710 Philips diffractometer, with graphite monochromated Cu Kα radiation. Infrared spectra were recorded on a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. The identification of phases was carried out by comparison with standard reference patterns from powder diffraction database stated by JCPDF and of a Clay Mineralogy Handbook [5,6].

3. Evolution of the phases on heating

The measurements of intensity variations of characteristic XRD peaks and FTIR bands of compounds are sufficient criteria to be used in comparisons in order to obtain a trend in the behaviour of similar mixtures. Instrumental conditions were maintained constant in order to obtain a better comparison of the intensities of the same XRD characteristic lines by using "batch program" analysis in PC-APD software (version 3.6). With the same aim a standard procedure was adopted for the preparation of the test specimens as in other works [7]. All the samples were ground the same time and uniform compaction was obtained using the same amount of powder and hand pressure in each case.

3.1. Diffraction results

Fig. 1a and b shows X-ray diffractograms of the S and P samples after heating at 150, 950, 1100 and 1200 °C.

XRD patterns of both specimens dried at 150 °C showed quartz (Q), illite (I)/muscovite (Mc) and kaolinite (K) as common crystalline phases. The differences between both types of slips were given by the presence of feldspar (albite) in the case of S slip, and calcite (C) in the sample proceeding from P slip.

With the purpose to study the trend in the behaviour of the mixtures and to get a deeper insight into the evolution of phases formed during firing the following principal reflections (in parenthesis) were used: quartz (3.3281 Å), muscovite (10 Å), illite (9.96 Å), kaolinite (7.0513 Å), calcite (3.035 Å), sodium feldspar-albite (3.1874 Å), anorthite (3.1805 Å) and mullite (5.3457 Å and/or 1.5240 Å). The last reflection was necessary to identify mullite at 1200 °C because the principal reflection (5.3457 Å) in P specimen, was hidden by the presence of amorphous silica (higher background about 22° 2θ).

The evolution of the different phases with temperature in the range 150–1200 °C was studied. After each thermal treatment, a semi-quantitative XRD analysis of the phases present was carried out by taking into account the peak intensity obtained by XRD with the appropriate software as stated before. The mineral content found related to the main final temperatures under study, is shown in Fig. 2a and b. It can be observed that:

The kaolinite becomes progressively less crystalline by dehydroxylation to form metakaolinite (MK, amorphous) at a low temperature, around 500 °C. Nevertheless, it was not possible to accurately establish the complete dehydroxylation by this technique because XRD can reveal little about the occurrence of poorly ordered material.

The illite and muscovite reflection were observed until 950 °C. The higher temperature of disappearance of these three-layer-minerals is attributed to crystalline structure persistence after the dehydroxylation [8].

The apparition of mullite (M) in both materials (S and P) and of anorthite in the specimen prepared from P slip was observed at 1100 °C.

At 1200 °C, quartz was still present in S and P. On the other hand, reflections from the other raw materials were not detected. This fact is related to the completely transformation of these minerals. A higher background, about 22° 2θ, was also observed, indicating the presence of amorphous silica.

Therefore, the specimen prepared from S slip showed the presence of glassy phase, quartz and mullite, whereas the other one, obtained from P type slip was composed of glassy phase, quartz, mullite and anorthite. The formation of anorthite only in the specimen proceeding from P slip was in agreement with the presence of calcite in the original slip. Bearing in mind that the mullite is formed at low temperature and directly upon clay minerals, it is possible to suppose that the mullite phase is primary [9].

3.2. FTIR results

For the determination of the mineral constitution the combination of X-ray diffraction and the Fourier transform infrared spectroscopy (FTIR) have proved to be suitable methods. With the help of vibrational spectroscopy, apart from good crystalline, also poor crystalline and amorphous inorganic components and organic substances can be identified.

The FTIR spectra obtained for S and P mixtures are in full agreement with XRD results. Typical bands assigned to kaolinite, illite or muscovite and quartz, the main minerals present in the raw materials, are distinguished in the IR spectra depicted in Fig. 3. All specimens were dried, previously to spectroscopic measurements, at 110 °C for a few hours, to avoid the presence of spurious water bands due to moisture, which could affect the fundamental OH stretching bands.

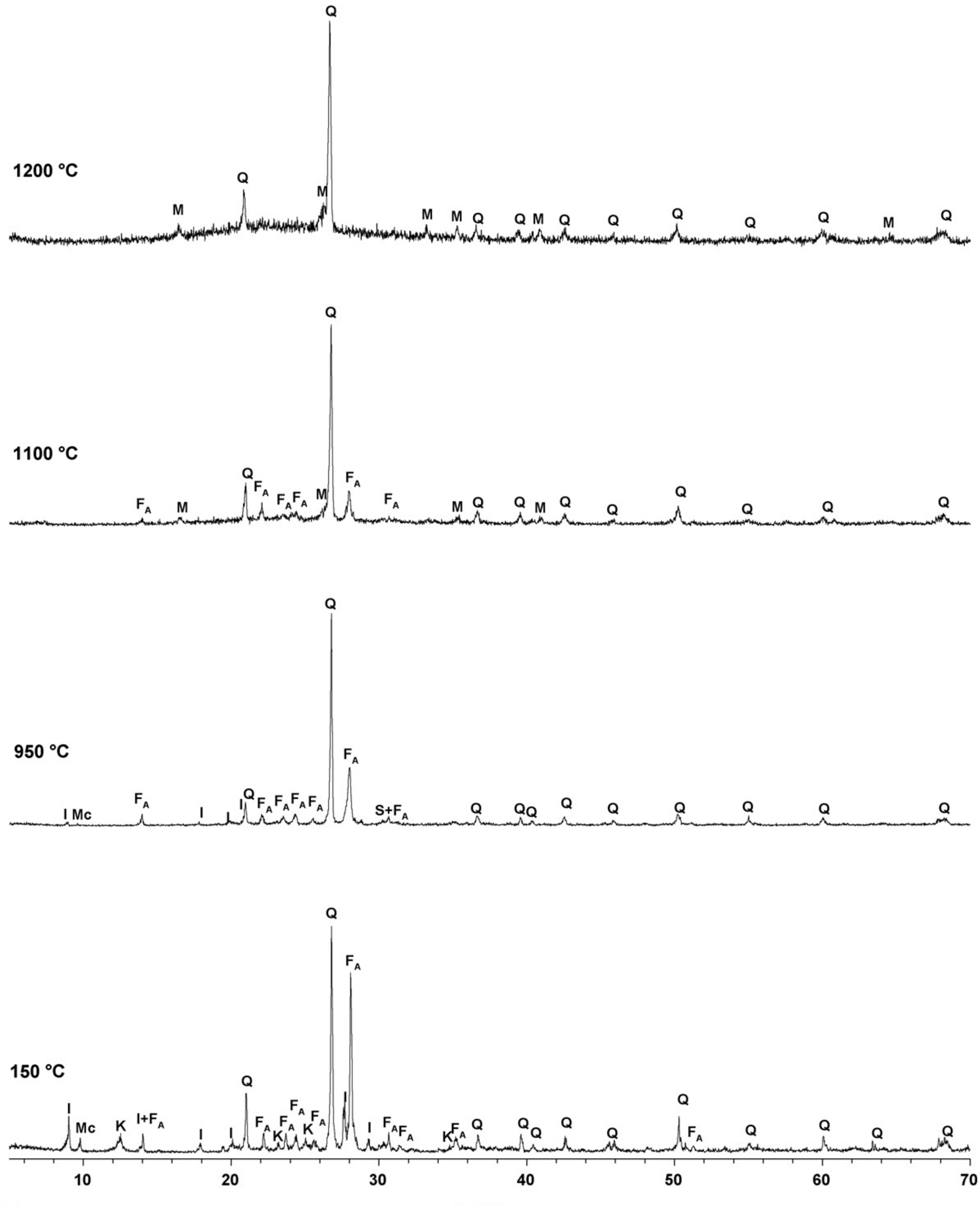

Fig. 1. (a) XRD pattern of S sample at different temperatures. I, illite; Mc, muscovite; K, kaolinite; FA, feldspar (albite); Q, quartz; s, spinel; M, mullite. (b) XRD pattern of P sample at different temperatures. I, illite; Mc, muscovite; K, kaolinite; Q, quartz; C, calcite; s, spinel; A, anorthite; M, mullite.

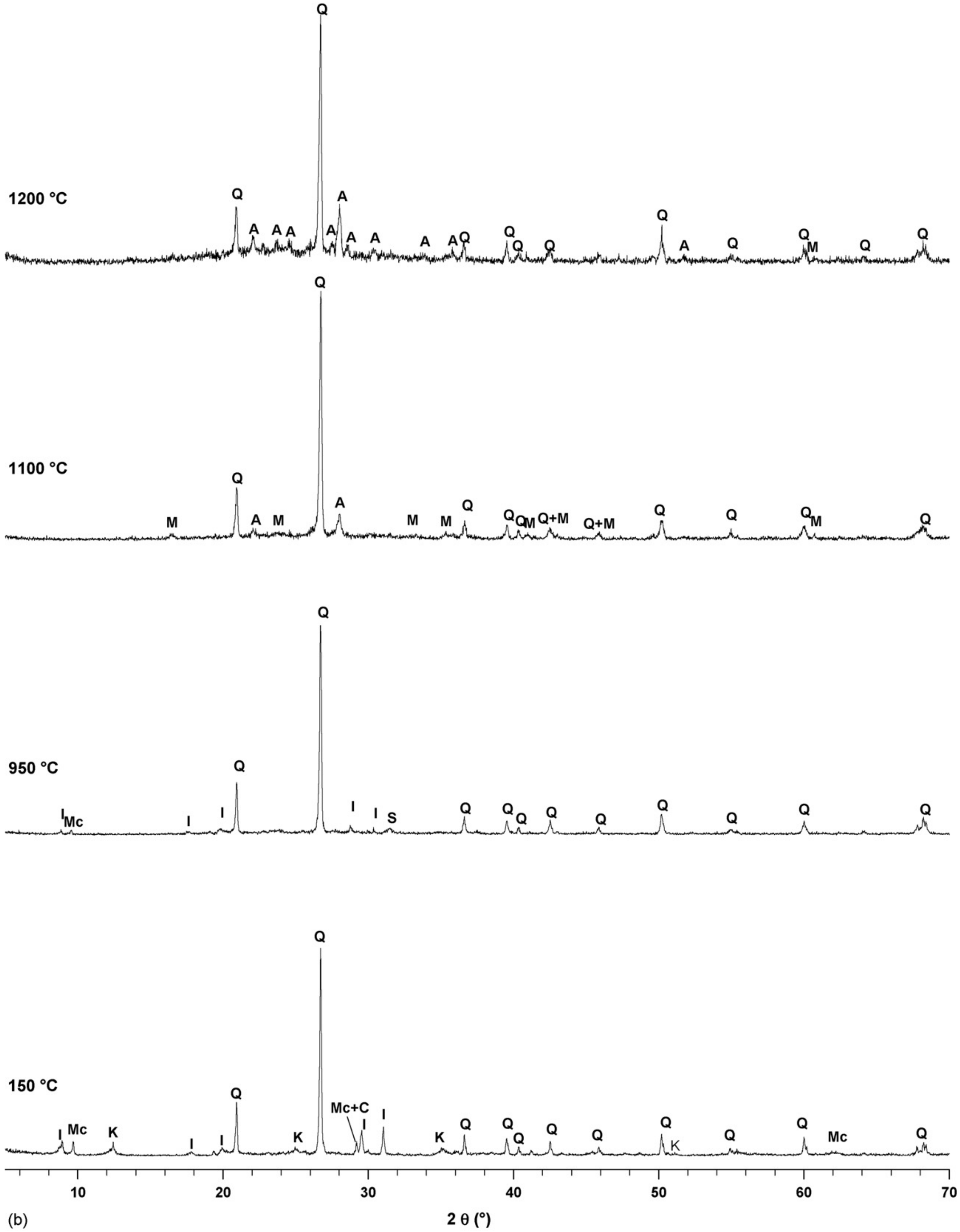

Fig. 1. (*Continued*).

Kaolinite can be readily distinguished by the 3700 and 3620 cm^{-1} doublets, assigned to OH stretching arising from inner and inner surface OH bonds. These absorptions, which usually lie well separated from those of the most other clay minerals, are characteristic of the kaolinite group. The resolution of these bands suggests a highly ordered well crystallized structure for this mineral [5].

On the other hand, the intense Si–O and Si–O–Al stretching frequencies lying at 1115–1008 cm^{-1} are consistent with the

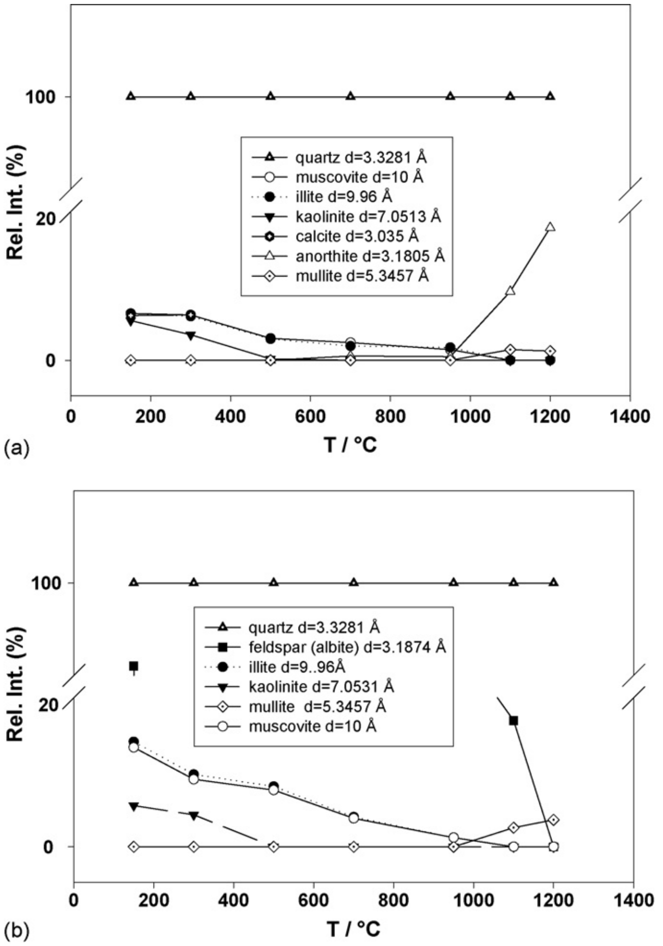

Fig. 2. (a) Changes in the mineral composition as a function of firing temperature, for P specimen. (b) Changes in the mineral composition as a function of firing temperature, for S specimen.

spectral pattern of kaolinite, as well as the doublet at 937–912 cm^{-1} attributed to Al–OH libration. However, characteristic bands belonging to quartz, feldspars and other clays are overlapping in the same region. Illite, frequently associated to muscovite, is clearly distinguished by the OH-stretching around 3620 cm^{-1}, accompanied by the broad absorption at 3400 cm^{-1}, although the weak step at 917 cm^{-1} is not observed in our spectra [10].

The sharp splitted band at 800 and 781 cm^{-1} is a diagnosis to identify quartz. In the low energy region, below 500 cm^{-1}, the vibration belonging mainly to deformation of SiO_4 and AlO_6 polyhedra of all constituents are not generally valuable for diagnosis due to their coupling. Only the sharp strong absorption at 535 cm^{-1} of kaolin minerals lies separated from the other components.

The comparison of both spectra shown in Fig. 3 allows to differentiate certain components in the S and P slips. In the case of S, extra bands assigned to feldspar albite are detected, although weak, at 763, 747, 724 and 649 cm^{-1}. They are not detected, though, in the case of P slip, while a very characteristic band of the asymmetric stretching vibration of CO_3^{2-} anions, at 1432 cm^{-1}, belonging to calcite is clearly observed in its spectra.

IR data for calcined samples at different temperatures were analyzed. The spectral patterns at most representative firing steps may be seen on Figs. 4 and 5. Up to 500 °C no significant changes are observed in the IR spectra of both materials. During this firing step the bands at 3700–3600 cm^{-1} are clearly modified due to dehydroxylation of kaolinite giving rise, as expected, to metakaolin. It was also found that dehydroxylation, between 500 and 700 °C, is accompanied by amorphization since the aluminosilicate sheets are disrupted [11]. On the other hand, the most intense band centered at 1000 cm^{-1} is slightly displaced toward higher wavenumber reflecting the increasing of Si–O–Si, Al–O–Al bonds along with the formation of new Si–O–Al ones. The characteristic Al–OH libration mode at 937–912 cm^{-1} is lacking. In P sample, the strong band, located in the low energy region, at 535 cm^{-1}, assigned to AlO_6 group [12,13], present in kaolinite is markedly weakened in accordance with XRD measurements.

After the heat treatment at 950 °C, the clays have almost completely lost OH groups. The shift toward higher frequency is noteworthy. The removal of OH groups in the sample results

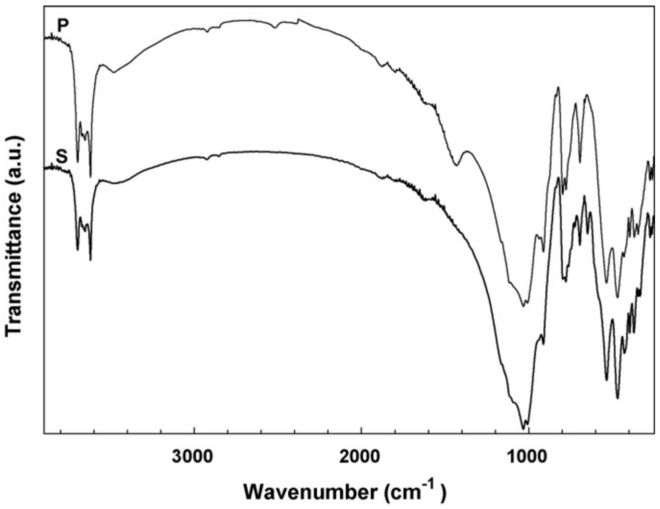

Fig. 3. FTIR of S and P slip treated at 150 °C.

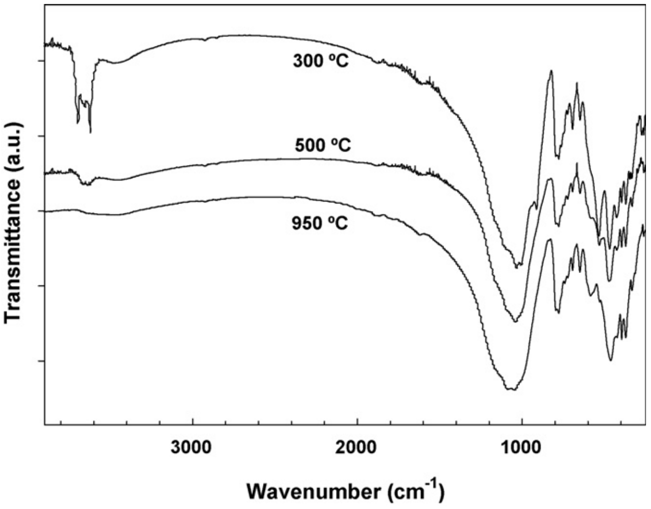

Fig. 4. FTIR spectra of S slip heated at different temperatures.

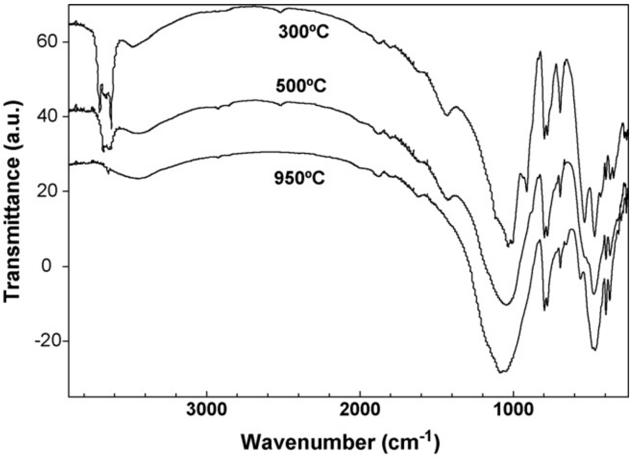

Fig. 5. FTIR spectra of P slip heated at different temperatures.

in the reinforcement of Al–O and Si–O linkages in the respective polyhedra of the aluminosilicate sheets and, in addition, in the formation of new Si–O–Al bonds by condensation of both polyhedra, as already stated. The loss of resolution in the 900–400 cm^{-1} region is due to the existence of agglomeration of aluminosilicates (and perhaps of SiO_2 and Al_2O_3) in the amorphous state.

In the case of sample P, CO_3^{2-} bands have disappeared due to thermal decomposition of calcite present in the raw material the same as the clay band located at 535 cm^{-1}, already mentioned. At the same time a new band at 562 cm^{-1} that could be assigned to AlO_6 stretching of Ca silico-aluminate could not be identified unambiguously. Nevertheless, we believe it is an intermediate phase formed by reaction of CaO and reacting clay, prior to anorthite formation, as will be explained later. The presence of a weak signal at 3643 cm^{-1}, characteristic of Ca–OH vibration in hydrated Ca silicates and Ca aluminates [14], suggests that the phase is highly reactive with atmospheric moisture. In this way, at 1100 °C, the major change in the spectra corresponds to the disappearance of 562 cm^{-1} absorption which evolves into the formation of a two band spectra, in the same region, located at 621 and 567 cm^{-1}, as well as a shoulder at 925 cm^{-1} as shown in Fig. 6. These could be confidently assigned to anorthite, as it has been already discussed for XRD pattern at this stage of reaction as a result of solid state reaction between CaO and clay. After the thermal treatment at 1200 °C, as may be seen in Fig. 6, anorthite bands increase their intensity since all Ca incorporated with calcite is stabilized in this synthetic phase. The rest of the spectrum is similar in its general features because the same phases are maintained. Characteristic mullite bands, between 900 and 500 cm^{-1}, are not detected surely due to low concentration (see Fig. 2a) and overlapping with other vibrations in the same spectral region.

On the other hand, for sample S, once the thermal treatment at 950 °C has been accomplished none of the typical clay bands are detected, but instead, two sharp bands are clearly observed at 585 and 530 cm^{-1}. These absorptions are essentially assigned to almost "pure" Al–O stretching of AlO_6 lattice present in the structure of the phase, commonly called spinel, which is the precursor of mullite development [15,16]. At this temperature, feldspar bands are still remaining in the spectra. The bands associated to "condensed" AlO_4-tetrahedra, expected in the range of 850–750 cm^{-1}, as found in numerous aluminates and related systems [13], are not observable probably because of their lower intensity and also by the partial overlapping and broadening of the strong band belonging to SiO_4 tetrahedra belonging to the rest of the phases present in the samples. The higher energy bands are not under discussion since in such frequencies are not clearly related to pure AlO_4 tetrahedra but rather to Si–O–Al mixed vibrations in aluminosilicates. At 1100 °C not significant changes are detected in the spectra as can be seen in Fig. 7. As feldspar is in coexistence with spinels, the formation of mullite is supposed to be primary, in accordance with XRD information. After the firing treatment at 1200 °C bands at 585 and 530 cm^{-1}, as may be seen in Fig. 7, are indistinguishable. They overlap into one broad absorption centered around 553 cm^{-1} assignable to AlO_6 octahedra present in mullite. The overlapping and broadness of Al–O band probably indicates a disordered distribution in this

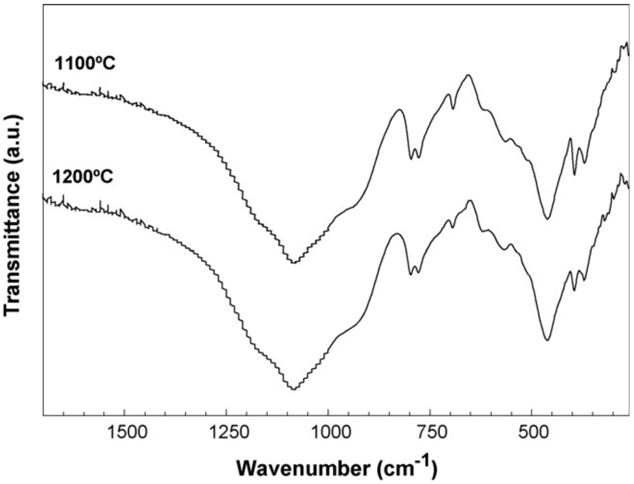

Fig. 6. FTIR spectra of P slip calcined at 1100 and 1200 °C.

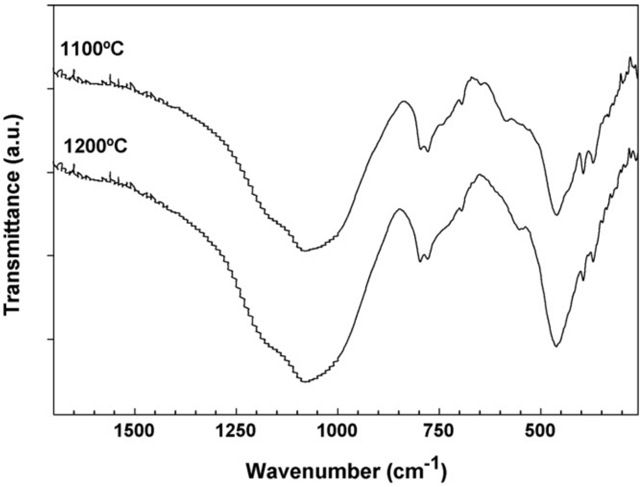

Fig. 7. FTIR spectra of S slip calcined at 1100 and 1200 °C.

material or short range order in the crystal structure [17]. Feldspar bands are undetected in the final thermal step.

4. Conclusions

Both analytical techniques, FTIR and XRD, applied to the developing of phases during firing process, are complementary, allowing a better evaluation of changes as well as the detection of phases present in the microstructure when an electronic microscopy is not available.

The degree of dehydroxylation may be better analyzed by FTIR. Dehydroxylation process is accompanied with the kaolinite amorphization. The kaolinite is fully dehidroxylated, in both materials at above 700 °C.

Al–O vibrations are more sensitive to the structural changes, since mullite and anorthite formation implies a change in the coordination polyhedra from "condensed" AlO_6 in aluminosilicate sheets of clays toward AlO_4 tetrahedra in the final firing phases; meanwhile SiO_4 tetrahedra are kept constant despite the rest of the environment be it either crystalline or semicrystalline. The analysis of the AlO_n "almost" independent vibrations, between 900 and 500 cm^{-1}, is more useful to evaluate the evolution of phases during the final steps of calcination. The high energy region of the spectra is less useful due to coupling of SiO_4 and AlO_4 polyhedra, though.

There is a clear relationship between the composition of the phases of the final ceramic product and the component present in the raw material when similar granulometry, firing program and furnace atmosphere are kept during the firing process of both materials. In the case of P slip, mullite and anorthite are formed, after clay and calcite decompose and react; this would be a calcium type pottery slip. On the other hand, S slip has a feldespatic composition, in which mullite forms from clays, acting interlaying K^+ from illite and feldspar as mineralizers.

FTIR spectra give additional support to XRD results because the mullite formed is primary.

Acknowledgement

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References

[1] W.M. Carty, U. Senapati, Porcelain-raw materials, processing, phase evolution, and mechanical behavior, J. Am. Ceram. Soc. 81 (1) (1998) 3–20 (and references therein).

[2] B. Baran, Y. Sarikaya, T. Alemdaroğlu, M. Önal, The effect of boron containing frits on the anorthite formation temperature in kaolin–wollastonite mixtures, J. Eur. Ceram. Soc. 23 (2003) 2061–2066.

[3] F.H. Norton, Elements of ceramics, second edition, Addison-Wesley Publishing Company, USA, 1974.

[4] M.P. Biondolillo, Manual Para el Ceramista, EDIUNC, Mendoza, Argentina, 2000.

[5] M.J. Wilson, A Handbook of Determinative Methods in Clay Mineralogy, Blackie & Son Ltd., London, 1987.

[6] R. Jenkins, Mineral Powder Diffraction File Data Book (JCPDS), Joint Committee on Powder Diffraction Standards, USA, 1986.

[7] A. Aras, The change of phase composition in kaolinite- and illite- rich clay-based ceramic bodies, Appl. Clay Sci. 24 (2004) 257–269.

[8] A. Khalfaoui, S. Kacim, M. Hajjaji, Sintering mechanism and ceramic phases of an illitic-chloritic raw clay, J. Eur. Ceram. Soc. 26 (2006) 161–167.

[9] K.H. Schüller, Reactions between mullite and glassy phase in porcelains, Trans. Br. Ceram. Soc. 63 (2) (1964) 103–117.

[10] J.L. Post, L. Borer, Physical properties of selected illites, beidellites and mixed-layer illite-beidellites from southwestern Idaho, and their infrared spectra, Appl. Clay Sci. 22 (2002) 77–91.

[11] A. Shvarzman, K. Kovler, G.S. Grader, G.E. Shter, The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite, Cem. Concr. Res. 33 (2003) 405–416.

[12] D. Voll, P. Angerer, A. Beran, H. Schneider, A new assignment of IR vibrational modes in mullite, Vib. Spectrosc. 30 (2) (2002) 237–243.

[13] P. Tarte, Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra, Spectrochim. Acta 23 A (1967) 2127–2143.

[14] J. Bensted, P. Varma, Some applications of infrared and Raman spectroscopy in cement chemistry, Cem. Technol. 5 (4) (1974) 378–382.

[15] P. Padmaja, G.M. Anilkumar, P. Mukundan, G. Aruldhas, K.G.K. Warrier, Characterisation of stoichiometric sol–gel mullite by fourier transform infrared spectroscopy, Int. J. Inorg. Mater. 3 (2001) 693–698.

[16] S. Satoshi, C. Contreras, H. Juárez, A. Aguilera, J. Serrato, Homogeneous precipitation and thermal phase transformation of mullite ceramic precursor, Int. J. Inorg. Mat. 3 (2001) 625–632.

[17] Y.F. Cheng, M.Ch. Wang, M.H. Hon, Phase transformation and growth of mullite in kaolin ceramics, J. Eur. Ceram. Soc. 24 (2004) 2389–2397.