

Microstructural characterization of sanitaryware by infrared and Raman spectroscopy, the role of vitreous matrix on properties

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Besides Raman and infrared spectroscopy, DSC/DTA/TGA, dilatometry, XRD, and SEM techniques were used to characterize phase transitions and microstructural evolution in porcelain stoneware. An experimental porcelain composition has been formed by slip casting and sintered in an electric furnace. Thermal evolution of raw materials shows dehydroxylation of kaolinite, transformation to spinel and mullite, and transformation of α -quartz into β -quartz evidenced by Raman spectroscopy. Spinel and granular (primary) mullite is seen to form in clay relicts which may subsequently become seeds for topotactic grown of acicular reinforcing mullite. As vitrification progresses the bridging silicon oxygen varies and can lead to connectivity changes in the silica network. The development of glassy matrix was followed by infrared spectroscopy at the porcelain intermediate sintering stage. Si-O-Si bands at 780 and 1070 cm^{-1} for symmetric and asymmetric stretching vibrations in the spectra have been analyzed using a polymerization index (PI). PI indicates the degree of depolymerization of the vitreous matrix through densification. PI was found to correlate well with thermal expansion, bulk density and Young's modulus. This correlation of glass structure and properties may suggest that changes in the IR spectra could be used to predict physical properties.

Key words: Microstructure, Infrared Spectroscopy, Raman, Sanitaryware, Glass ceramics, Polymerization Index.

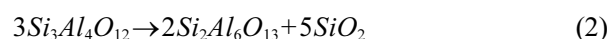
Introduction

In general, porcelain is composed primarily of clay, feldspar and quartz which are heat-treated to form a glassy matrix and crystalline phases such as mullite and quartz. At about 550 °C dehydroxylation of hydroxyl clay groups occurs to form metakaolin ($\text{Al}_2\text{Si}_2\text{O}_7$) through an endothermic process, but continuous hydroxyl loss (OH) is observed up to 900 °C and has been attributed to gradual dehydroxylation of metakaolin [1]. Further heating to 925-950 °C converts metakaolin to a defect aluminum-silicon spinel, $\text{Si}_3\text{Al}_4\text{O}_{12}$, this is also referred to as a gamma-alumina type structure and amorphous free silica:



Feldspars are low-melting mineral alkali aluminosilicates and serve as a viscous liquid phase. The liquid phase reacts with other body constituents and gradually permeates the microstructure, leading to densification [2-4]. Amorphous free silica is highly reactive and possibly assists potassium in the feldspar eutectic reaction at about 990 °C.

Upon calcinations to ~ 1050 °C, the spinel phase nucleates and transforms topotactically to mullite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) 1 : 1 and crystalline cristobalite:



The morphology and stoichiometry of mullite may be obviously influenced by the starting materials and processing technique. It is known, for example, that stoichiometric mullite only forms from oxide precursors at high temperatures, whereas non-stoichiometric $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ mullite derives only from melt-derived systems [6, 7]. Porcelain bodies generally contain two different mullite types i.e. primary and secondary, whose details of formation are controversial. The mullite precursor unstable spinel phase transforms to orthorhombic mullite at 1075 °C. Furthermore, the chemical nature of precursory phases can modify the temperature of mullite formation. Primary Mullite can form on the surface of kaolinite relicts [8], that in turn serves as a seed for crystallization of the secondary mullite needles as alkali diffuses out of feldspar at higher temperatures [2, 3, 9]. Tertiary mullite has been reported in aluminous porcelains precipitating out of alumina-rich liquid [2, 7]. Mullite as a porcelain reinforcing phase affects the mechanical properties due to its acicular morphology and stress generated in the glassy matrix due to the expansible nature of its formation. Baudín and Villar [10] studied

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the influence of the thermal treatment within the range of 900-1630 °C, on the microstructure of the 3 : 2 mullite in the presence of a low content of alkaline oxides. They concluded that the presence of 0.28 wt.% ($\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}$), as main impurities, enables a microstructural development, which comprises three main steps: dissolution of mullite grains; formation of a liquid phase; and the grain growth from the liquid phase. As the temperature increases, the grain growth from the liquid phase overlaps the dissolution of mullite grains and a bimodal microstructure develops, with an increasing fraction of acicular mullite. The starting compositions, and especially the alumina/silica ratio, determine the evolution of mullite crystals growth. Furthermore, the mullitisation reaction process is accomplished at lower temperatures if the proportion of alumina in the sample is above the stoichiometric composition of mullite. On the other hand, if the alumina content is too high, the excess might undergo structural rearrangements and give rise to the formation of α -alumina.

Quartz, when it is fired to high temperature, results in substantial quantities of viscous glass. Quartz is readily transformed into cristobalite only at temperatures between 1470 °C and 1710 °C [5]. There is a controversy about whether the quartz-cristobalite transformation is a direct process or necessitates the presence of an intermediate amorphous or liquid phase. Chen *et al.* [11], reported for $T > 1200$ °C, that amorphous silica gradually transforms into cristoballite, while at $T > 1500$ °C, cristoballite transforms again into amorphous silica. Extensive research on porcelain has been going on for decades, only to confirm its complexities and reiterate the important challenges in understanding porcelain in relation to raw materials, processing science, phase equilibrium, and microstructural evolution.

IR and Raman spectroscopies are valuable tools for studying on a molecular scale the structural transformations which progressively occur during vitrification. These techniques have been extensively used in recent years for the study of silica and ceramic glasses [12-16]. Ceramic glasses are aluminosilicate networks in which SiO_4 tetrahedra are joined together by oxygen atoms located at the vertices. The silicate structural unit is the silicon-oxygen tetrahedron which contains a varying number of non-bridging oxygens depending on the alkali content of the glass. The well known structural model of glass formation is that due to Zachariasen [17, 18]. Specifically, a shift of the Si-O stretching band in IR spectra is used to monitor changes in average Si-O-Si bond angle in the glass structure [12-16]. A clear differentiation between various glasses is possible, because the connectivity of the SiO_4 polymeric units can be investigated through the relative spectral intensities of Si-O stretching and bending modes, respectively [12-16]. Different spectral components (Q^n for stretching components, Q^n for

bending ones) have been assigned in the literature to the vibrations with zero (Q^0 or monomer, i.e. isolated SiO_4 , ca. 800-850 cm^{-1}), one (Q^1 or Si_2O_7 groups, ca. 950 cm^{-1}), two (Q^2 or silicate chains, ca. 1050-1100 cm^{-1}), three (Q^3 or sheet-like region, ca. 1100 cm^{-1}) and four (Q^4 , SiO_2 and tectosilicates, ca. 1150-1250 cm^{-1}) bridging oxygens [15]. Pérez *et al.* [16], studied by Raman and IR spectroscopies the grinding process of vitreous silica and a conventional glass by using the polymerization index (PI). The PI indicated various depolymerization levels achieved on the particle surface after grinding, and concluded that depolymerization results from the breakage of the Si-O-Si bonds. The PI was calculated from the spectra by the relative changes in the symmetric and antisymmetric Si-O-Si bands area ratios at 1100 and 800 cm^{-1} . Tamayo *et al.* [19], recently in the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ glass system studied by Raman and IR, showed that PI decreases with B concentration except for low boron content glasses. They established the polymerization index gives structural characterization of glasses. Structural characterization gives evidence for the formation of three and four bridging oxygens in the silica tetrahedral group. Falcone *et al.* [20] in the characterization of Al-rich glass refractory interfaces, give a supporting method for analysis of stones in industrial glass production by SEM-EDX and Raman spectroscopy. They proved that Raman is a complementary technique to outstanding phase formations and distribution inside Al-rich zones in glass. Shartsis *et al.* [21] discussing physical properties of molten alkali silicates, plot the viscosity dependence of temperature up to 1400 °C together with increasing alkali concentrations, finding an analogous tendency of viscosity under the influence of either temperature or alkali concentration. Regarding structural evolution of porcelain, Lavat *et al.* [22], studied phase changes of ceramic whiteware by XRD and FTIR showing that Al-O vibrations are highly sensitive to the structural changes during porcelain firing. They further showed that IR spectra provided additional structural support to XRD while examining microstructural evolution.

It is widely known in the literature [12-16, 19, 20] that IR spectroscopy can be used to interpret glass structural changes and further confirmed that similar structural changes would produce similar changes in glass properties. Therefore, monitoring the IR spectra of a glass sample can be used to deduce changes in glass properties. In this work, the porcelain glassy matrix development has been closely examined as vitrification progresses by following the polymerization index behavior at the intermediate sintering stage. Chemical changes by the Al-O, Si-O IR and Raman spectral vibrations gave evidence on mullite, quartz and glass phase evolution. It has been proved that Si-O spectral vibration modes do change as stoneware vitrification develops and that such changes can be

related to the properties of the sanitaryware. *In situ* densification and major thermal phase changes were followed by dilatometry and DTA, respectively. Phase changes from spinel to primary and secondary mullite, were characterized by means of EDX, and secondary electrons.

Experimental Procedure

Experimental composition of porcelain stoneware were prepared out of clay, feldspar and quartz (50 : 40 : 10 wt %). Rectangular $120 \times 25 \times 10$ mm samples were formed by slip casting and sintered in an electric furnace. Green body compositions consist of 66.62 wt % SiO_2 , 24.76 wt % Al_2O_3 , 0.63 wt % Fe_2O_3 , 1.03 wt % TiO_2 , 0.29 wt % CaO , 0.12 wt % MgO , 3.18 wt % Na_2O and 3.26 wt % K_2O . DTA tests were carried out in a New Castle instrument Model Q600 running up to 1300°C , at 10 Kminute^{-1} , with $100\text{ cm}^3/\text{min}$ nitrogen gas flow. In-situ shrinkage was recorded by a Theta dilatometer Model 3230, up to 1300°C at a 10 Kminute^{-1} heating rate.

The samples were dried for 48 h in air and then at 110°C for 24 h in an electric furnace. Heating in the specimens was carried out with rates of 10 Kminute^{-1} , to 600, 1000, 1050, 1100, 1150, 1200, 1250 and 1300°C and kept at the maximum temperature for 0 to 120 minutes and cooling rates were also 10 Kminute^{-1} . Ten bodies had been fired at the indicated temperatures; the corresponding tests were carried out in order to determine their physical properties. Bulk density was measured by Archimedes method according to ASTM designation C 373-88. Elastic modulus of the ceramic bodies was determined by the grindosonic method according to the ASTM designation C 1259-98.

For SEM analysis, specimens were previously polished to a mirror surface by standard techniques and chemically etched with a 5% HF solution in order to dissolve the glass and reveal the mullite phase. A Jeol JSM-6400 SEM, at 15 kV coupled with an EDS detector (Bruker AXS Inc. XFlash 4010), was used for microstructural observations in order to distinguish the various phases and their chemical composition. A TENSORTM 37 series FT-IR (Bruker Optics Inc), was performed to obtain infrared spectra by ATR technique (with ZnSe crystal), spectra were accumulated over 64 scans at 2 cm^{-1} of resolution. Raman spectrometer used is a Dilor Lamram 2, at a 514.5 and 632.8 nm lines, from an Ar and HeNe ion laser excitation at 15 and 20 mW. Deconvolution of peaks and the area of the bands in the spectra analyzed was calculated by Origin software peak-fitting module (Microcal Software, Inc.) and PeakFit v4.00 software (AISN INC). The depolymerization index was calculated using a ratio $1070/780\text{ cm}^{-1}$, corresponding to asymmetric stretching vibrations of Si-O bonds in the SiO_4 network and the bending symmetric vibrations of the Si-O-Si, respectively.

X-ray diffraction analysis used a Siemens D5000 with Cu $\text{K}\alpha$ radiation 1.54 at 20 KV.

Results and Discussion

Sintering

Fig. 1 shows the DTA and linear shrinkage behavior. An endothermic peak at 150°C , is due to the removal of physically adsorbed water followed by dehydroxylation of kaolin and the loss of absorbed water at 494°C . The broad endothermic band around 580°C is due to the $\alpha \rightarrow \beta$ quartz transformation. The exothermic peak at about 990°C is due to the transformation of metakaolin to a spinel-type structure and mullite [2, 23, 24]. The $1200\text{--}1300^\circ\text{C}$ endothermic effect during sintering is due to the formation of a liquid phase derived from the feldspar component. The dilatometric curve shows three sintering stages i.e. initial, intermediate and final step. A negligible shrinkage is observed up to 1100°C during initial sintering. At the intermediate stage a most densification starts by the $\text{K}_2\text{O}\text{--Al}_2\text{O}_3\text{--SiO}_2$ eutectic formation (1100°C). The widespread occurrence of glass at this stage may influence most of the shrinkage shown by the dilatometric curve. Judging by the extent of shrinkage of the dilatometric curve, densification develops into a fully vitrified body up to 1225°C . The derivative of the shrinkage curve is shown in fig. 1 indicating the maturing temperature of the body at about 1225°C [25].

XRD patterns show the mineralogical composition of raw materials i.e. quartz (Q), anorthoclase feldspar (A), kaolinite (K) and spinel formation at 1100°C in the initial stage of densification reported in previous work [27]. Fig. 2 shows infrared spectra of the raw materials without heat treatment where are observed quartz, anorthoclase feldspar and clay phases. The 3693 , 3653 and 3620 cm^{-1} triple peaks could be assigned to OH stretching arising from inner and inner surface OH

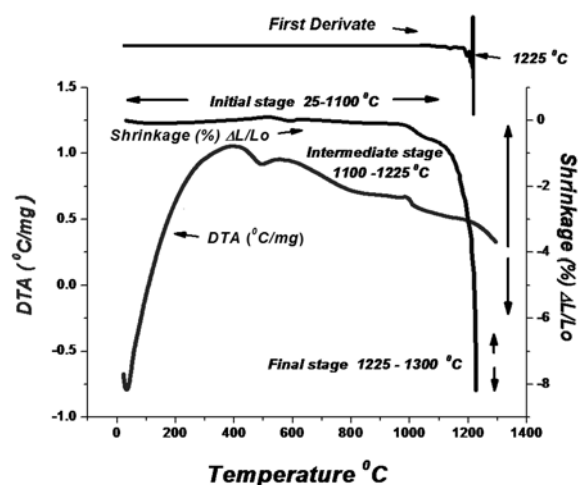


Fig. 1. Thermal dilatometry and DTA for an experimental sample sintered up to 1300°C at 10 Kminute^{-1} . Note most of the shrinkage takes place at the intermediate sintering stage.

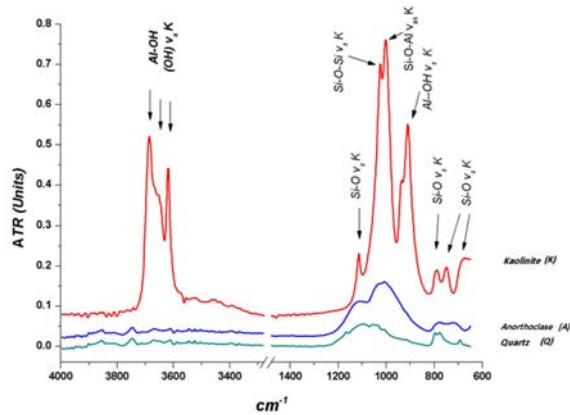


Fig. 2. Infrared spectra from the constituent raw materials at 25 °C (quartz, anorthoclase feldspar and clay). Peaks labeled as Q are alpha quartz, K, kaolinite and A, anorthoclase.

bonds in the kaolinite [1]; At the same time kaolinite exhibited the Si-O and Si-O-Al intense stretching bands lying at 1114 and 1004 cm^{-1} , as well as 912 cm^{-1} attributed to Al-OH. Two doublets bands at 1101, 1050 and 798, 773 cm^{-1} are assigned to quartz. The 1111, 1033, 1005, 779 and 719 cm^{-1} signal correspond to anorthoclase feldspar (see Table 1).

Fig. 3 shows the dissolution of sanidine in the range 1150-1200 °C as well as mullite appearance at 1150-1250 °C, quartz starts to dissolve within the vitreous matrix at 1150 °C reaching the (101) peak minimum at 1300 °C corresponding to maximum quartz dissolution. Mullite also appears to dissolve in the glassy phase at temperatures higher than 1250 °C as seen by the (120) mullite diffraction plane in fig. 4. The SEM micrograph confirms the dissolution of mullite by measuring the aspect ratio of the mullite acicular crystals, in etched specimens with HF, the acicular crystals aspect ratio decreases considerably at temperatures higher than 1250 °C. Finally, mullite dissolution at temperatures

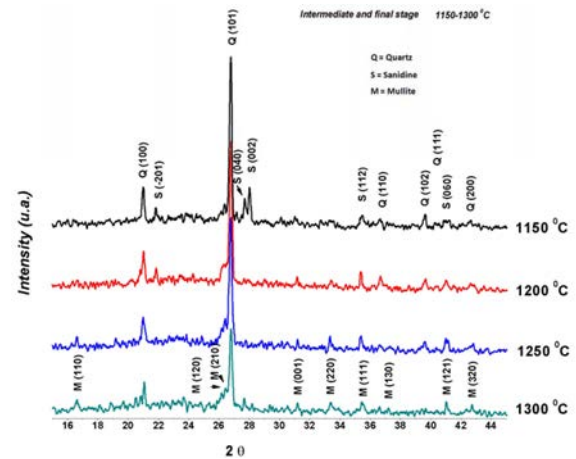


Fig. 3. XRD patterns of porcelain stoneware at increasing stages of densification. K = kaolinite, Q = quartz, A = anorthoclase, S = sanidine and M = mullite.

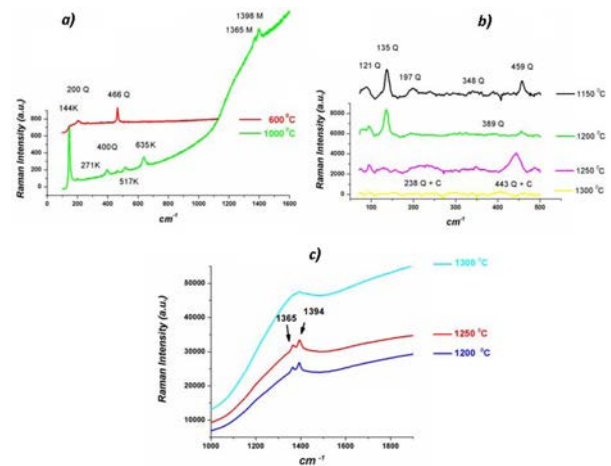


Fig. 4. Raman spectra showing porcelain phase evolution with temperature: a) initial stage 25-1100 °C, b) intermediate and final stage (1100-1300 °C), and c) mullite evolution at the intermediate and final stages. Q = alpha quartz, K = kaolinite, A = anorthoclase feldspar, M = mullite and C = cristobalite.

Table 1. Band positions in the infrared spectra of porcelain phases.

Structure	Wavenumber (cm^{-1})	Assignment	Structure	Wavenumber (cm^{-1})	Assignment
Kaolinite	3693	(O-H) Al-OH v_s	Kaolinite	1004	Si-O-Al v_{as}
Kaolinite	3653	(O-H) Al-OH v_s	Mullite	988	Si-O v_s
Kaolinite	3620	(O-H) Al-OH v_s	Kaolinite	912	Al-OH v_b
Kaolinite	3450	(O-H) H ₂ O v_s	Mullite	927	Si-O v_s
Kaolinite	1629	(O-H) H ₂ O v_d	Mullite	909	Al ^{iv} -O v_s
Mullite	1168	Al ^{iv} -O v_s	Mullite	828	Al ^{iv} -O v_s
Quartz	1165	Si-O v_s	Quartz	798	Si-O v_b
Mullite	1131	Si-O v_s	Kaolinite	795	Al-O v_s
Kaolinite	1114	Si-O v_s	Quartz	776	Si-O v_s
Mullite	1107	Si-O v_s	Feldspar	776	Si-O v_s
Quartz	1105	Si-O v_s	Kaolinite	745	Si-O v_s
Feldspar	1105	Si-O v_s	Mullite	737	Al ^{iv} -O-Al ^{iv} v_b
Quartz	1050	Si-O-Si v_s	Feldspar	719	Si-O-Al v_s
Feldspar	1029	Si-O-Si v_s	Quartz	690	Si-O v_s
Feldspar	1005	Si-O-Al v_{as}	Kaolinite	681	Si-O v_s

higher than 1250 °C is also shown by Raman spectroscopy in fig. 4, where it is seen that the 1365 and 1395 cm^{-1} mullite vibrations practically disappear from the spectra. This dissolving effect of mullite into the glass and therefore the partial disappearance of the mullite reinforcing phase may bring about a detrimental effect on the physical properties of porcelain [24, 25].

Fig. 4. shows Raman spectra for experimental porcelain samples subjected to increasing heating temperatures. The main bands at 144, 271, 517 and 635 cm^{-1} are attributed to the kaolinitic phase (Fig. 4-a). The band at 141 cm^{-1} has not been assigned yet to a vibrational mode; however, it's very large Raman intensity could occur only as a result of a mode which induces a very large change in polarizability [26]. The formation of mullite from kaolinite is markedly weakened in accordance with XRD and SEM observations, but Raman spectroscopy give additional information of the formation of mullite at 1000 °C. The characteristic bands of mullite appear at 1365 and 1399 cm^{-1} , corresponding to octahedral $\text{Al}^{\text{vi}}\text{-O}$ and higher intensity bands as mullitization progresses from the spinel phase precursor [27]. Also, a higher definition of the bands is observed to 1250 °C, which indicates a larger organizing of this phase when attaining this temperature, which turns out to be secondary, according to SEM. The partial dissolution of mullite in the liquid phase at 1300 °C is denoted by the small intensity of the mullite bands (see Fig. 4-c), meaning that mullite probably dissolves back into the glass at temperatures higher than 1250 °C. This suggestion is backed by the SEM observations on the reduced aspect ratio of acicular mullite as discussed above. Characteristic Raman bands of quartz and cristobalite are observed in the spectra of fig. 4-b. Cristobalite was observed at about 1250 °C, indicating thermal transformation of quartz. The maximum intensities of the cristobalite and quartz band absorptions are at 443 and 459 cm^{-1} , respectively. It is reported that the cristobalite band at 443 cm^{-1} only appear at high-temperatures [5], denoting the importance of the liquid phase in the transformation of cristobalite at low temperature. The partial dissolution of quartz and cristobalite in the liquid phase at 1300 °C is denoted by the small intensity of their characteristic bands.

Phase evolution upon firing (25-1300 °C) can be systematically followed by IR analysis as shown in Fig. 5 and characteristics bands of the raw material and final phases are shown in table 1. The sample fired at 600 °C shows a slight decrease in kaolinite intensity bands due to dehydroxylation, the characteristic bands at 3693, 3653, 3620, and 933-910 cm^{-1} are clearly modified and disappear. Asymmetric stretching vibrations of Si-O bonds in the SiO_4 network at 1070-1030 cm^{-1} are attributed to the glass phase at 1100 °C. The shoulder around 940 cm^{-1} can be ascribed to symmetric stretching vibrations of Si-O bonds, while that at 750-790 cm^{-1} corresponds to the symmetric vibrations

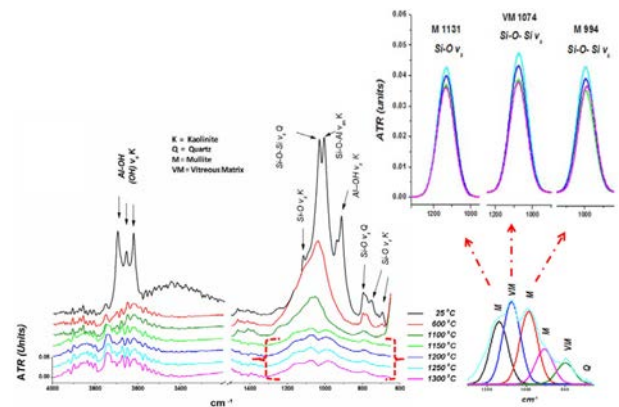


Fig. 5. Infrared spectra showing the evolution of porcelain phases with temperature. The bands were deconvoluted on the right side of the spectra to show the mullite (M), quartz (Q) and vitreous matrix (VM) bands.

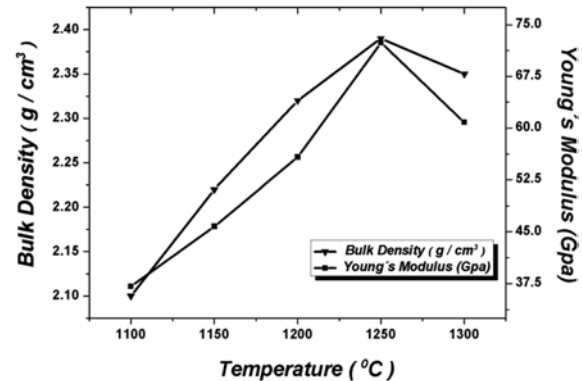


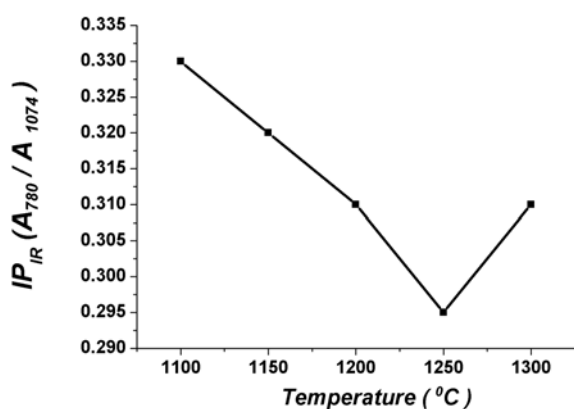
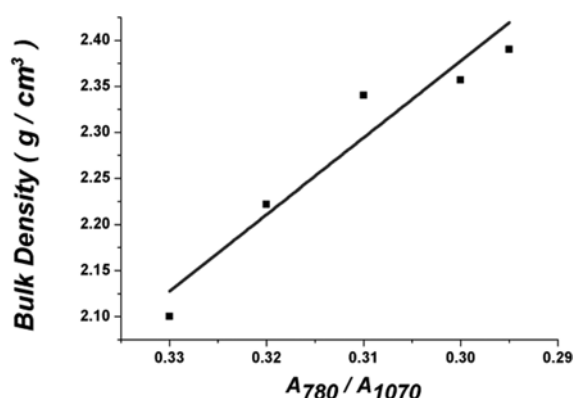
Fig. 6. Bulk density and Young's modulus against temperature for the experimental composition.

of the Si-O-Si or Si-O-Al bonds [12-16]. Characteristic mullite bands also appear at 1100 °C, for the 1131, 994 cm^{-1} spectral region corresponding to the tetrahedral $\text{Al}^{\text{iv}}\text{-O}$ bands. The increasing amount of glassy phase can be seen by the increasing intensity of the asymmetric stretching vibrations for the Si-O-Si bonds at 1074 cm^{-1} on the deconvoluted bands shown in fig. 6. It can be further seen that such band intensity goes up to a maximum at 1250 °C and decreases back to 1300 °C. This effect is important since 1250 °C is a key temperature that corresponds to a turning point in physical properties. Deconvoluted bands for the mullite show an increasing amount of the mullite phase up to 1250 °C. A higher definition of the bands is observed at 1250 °C, which turned out to be secondary mullite. The partial dissolution of mullite in the liquid phase at 1300 °C is denoted by a decrease in intensity of the mullite bands, backed up by SEM analysis.

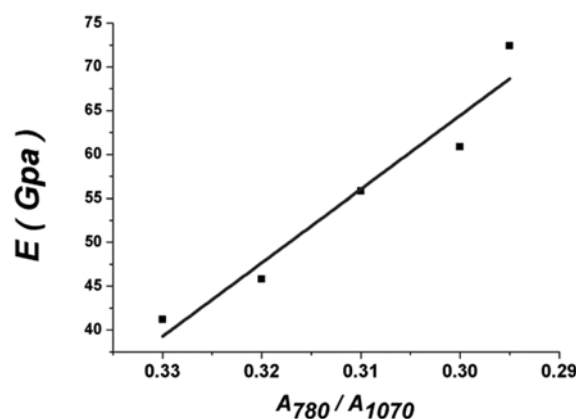
Fig. 6 shows the temperature dependence of bulk density and Young's modulus during the intermediate and final sintering stage. It is seen that maximum values of bulk density and Young's modulus are reached at 1250 °C and decrease at higher temperatures. Table 2, shows a higher level of bulk density and Young's modulus at 1250 °C, e.g. 2.39 g/cm^3 and 72.40 GPa,

Table 2. Mechanical properties and polymerization indices of a ceramic body as a function of the temperature of treatment.

Temperature (°C)	ρ (g/cm ³)	E (GPa)	MoR (MPa)	Linear Shrinkage (%)	Apparent Porosity (%)	IP-IR (I_{1070}/I_{780})
1100	2.10	37.1	20.88	5.18	1.69	0.33
1150	2.222	45.80	28.01	7.10	1.34	0.321
1200	2.340	55.81	36.27	8.76	0.61	0.304
1250	2.390	72.40	40.57	9.20	0.45	0.294
1300	2.357	60.85	37.94	8.03	3.20	0.297

**Fig. 7.** IR Polymerization index against temperature showing depolymerization of vitreous network up to 1250 °C. The degree of vitrification of a ceramic body is a function of the time and temperature of the treatment which the body has undergone.**Fig. 8.** Correlation of polymerization indices with the bulk density of porcelain.

respectively. An increment of the temperatures led to an increase in the properties. This increase can be explained by a decrease of the porosity and the increment in acicular mullite previously discussed. Bending strength depends on the crystalline phase content and is directly related to the increment of mullite and glass. Bloating also occurred at higher temperatures and led to an elevation of the apparent porosity and a decrease in the density and Young's modulus. Linear contraction, Young's modulus and bulk density were maximized at 1250 °C and 120 minutes. This temperature was considered to be ideal to fire this porcelain. The relationship between the mineralogy of the raw materials and phase changes taking place during their sintering under different conditions has been

**Fig. 9.** Correlation of polymerization indices with the Young's modulus of porcelain.

examined. Between 1100 and 1150 °C a considerable decrease in the porosity occurs, coinciding with the beginning of vitrification. A considerable decrease in the porosity therefore also begins. At 1250 °C the bodies become more vitrified and the pores close, and the porosity decreases significantly (table 2). This effect is developed by vibrations of the silica network in the IR spectra, the spectra shows the increase in the content in liquid phase and the decrease in its viscosity.

Correlation of depolymerization indices to physical properties

A polymerization index can be worked out by relating area changes of the symmetric and anti symmetric Si-O-Si bands (1100 and 800 cm⁻¹) on the IR spectra, as suggested by Pérez *et al.* [16]. Fig. 7 shows a plot of the polymerization index (PI_{IR}) versus densification temperature showing a decreasing index from 0.331 at 1100 °C to 0.295 at 1250 °C. This might be due to breaking of the alkaline glass silicon bonds brought about by temperature. At higher temperatures (1250-1300 °C), the index value increased back to 0.310. Presumably, the glass network polymerizes back by the influence of the silicon and aluminum dissolving action as discussed above, both being glass forming ions.

It is seen that maximum values of the bulk density and Young's modules are reached at 1250 °C and decrease at higher temperatures. Such a maximum is coincident with the minimum in the IR polymerization indices at the same temperature (1250 °C). Figures 8

and 9 show the correlation of the PI by IR versus physical properties of the porcelain body. It can be seen that high correlations are attained for the porcelain glassy matrix polymerization indices and ceramic bulk density and Young's modulus. It appears that polymerization structural changes are directly linked to the change in properties. It is interesting to note that the glassy matrix silica network thermal loosening up, is reflected by the respective spectral bands. Such glass network structural changes may be related to vitrification mechanisms.

Conclusions

Depolymerization of the vitreous matrix was assessed from the polymerization index. Depolymerization reached a minimum ($PI = 0.295$) at 1250°C and 120 minutes soaking time. It was shown that as the temperature increased within the intermediate sintering stage the glass network was disrupted up to 1250°C , however, the opposite effect took place between 1250°C and 1300°C . Such an effect on the alkaline silica vitreous matrix was apparently driven by the increasing sintering temperature higher than 1250°C , and it was apparently caused by the dissolving action of silica and redissolution of mullite. Depolymerization of the vitreous matrix provides additional evidence for the mechanism of densification by viscous flow since the polymerization index correlates well with both the increasing density and shrinkage within the intermediate sintering stage. Porcelain glass matrix structural parameters based on IR spectroscopy allowed one to follow depolymerization phenomena as related to physical properties corresponding to the intermediate sintering stage of the experimental sanitaryware composition. Polymerization indices attained a minimum at 1250°C and reversed back at higher temperatures meaning a breakdown in the silica polymeric structure at 1250°C and a partial repolymerization brought about by the silicon and aluminum dissolution into the glass. It appears that such structural changes were reflected in the porcelain physical properties.

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