ON THE GLASSY PHASE IN TRI-AXIAL PORCELAIN BODIES

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ABSTRACT
Porcelain bodies contain 40-60 vol.% of glass. The varying composition of glassy phase greatly influences mechanical properties, translucency and firing temperature of the final ceramic product. Despite the melting temperature of at least 1100°C, of the low melting flux present in the body, glass formation begins at a temperature lower than 1000°C. Experimental results have been explained on the basis of predictions from the K2O-Al2O3-SiO2 phase diagram. Initially, the amount of the liquid phase increases with increase in firing temperature due to the melting of feldspar. Silica discarded from clay relict during mullite formation at ≥1000°C and partial quartz dissolution at commercial firing temperatures also contribute to the glassy phase. The composition of glass close to quartz grains and within clay relics is highly silica-rich. The alkali content is sometimes higher in the matrix but heterogeneous in general due to inhomogeneous mixing of the initial body ingredients and inhomogeneous crystallization in various micro-regions. The variation in the size of mullite crystals observed in various micro-regions of the body is related to the viscosity of the constituent glass. The cracking of quartz grains has been discussed in terms of the thermal expansion mismatch of the constituent phases and cristobalite formation.

INTRODUCTION
Porcelains being vitreous ceramics are widely used in dinnerware, sanitary ware, decorative ware, electrical insulators and have applications in medicine and dentistry. The easy and cheap availability of the relevant raw materials and the simplicity of tools required for processing and body preparation have made porcelain manufacturing or pottery-making a favourite business since the prehistoric times. Because of widespread use of porcelain, interest in investigation relating to improvements in processing, forming and firing techniques have kept the white-ware industry equally operational in all parts of the modern world 1-6.

Porcelains typically comprise of 50 wt% clay (kaolinite, [Al2Si2O(OH)2]), 25 wt% flux and 25 wt% filler. The clay content when wet acts as a binder for the other body ingredients in the green state. It confers plasticity upon the body for moulding and shaping. Kaolinite transforms to meta-kaolin at temperatures ranging from 420°C to 660°C probably depending upon the amount and nature of the alkali content or other impurities present 7-12. Meta-kaolin transforms to α-Al2O3 type spinel, just before the beginning of crystallization of primary mullite at about 1000°C. In the final fired product, mullite crystals are believed to act as crack diverting flaws in the body 13. The fluxing material is usually low melting alkali silicates such as nepheline syenite and other soda or potash feldspars. Feldspar reacts with other body ingredients upon firing to form enough liquid or glass at commercial firing temperatures (~1200 to 1300°C). The resulting liquid fills the gaps and voids in the microstructure leading to densification of the body. The filler is relatively stable at commercial firing temperatures and reduces the tendency of distortion and shrinkage of the body. Fine grained quartz sand and/or alumina is used as filler to improve mechanical properties. Firing of triaxial porcelain bodies containing clay, flux and filler results in a grain and bond type microstructure. The granular phases are relatively coarse α-quartz or corundum grains, cuboidal primary mullite crystals and elongated (sometimes granular) secondary mullite crystals, and the bonding phase is highly heterogeneous glass matrix 14. Iqbal and Lee 15-16 used X-ray diffraction, scanning and transmission electron microscopy to investigate the phase and microstructural evolution in commercial as well as model porcelain systems. As a result the formation of various crystalline phases namely, primary, secondary and tertiary mullite were reported.

Vitrification means a high degree of melting upon firing. The formation of about 40 to 60 vol.% of glass leads to reduction in porosity and enhanced densification of the body 15. Therefore, improvement
in the mechanical properties, translucency and lowering of the sintering temperature of porcelain products can be achieved by changing the constituent glassy phase. Additionally, the glassy phase is present in every micro-region of the body and is more flexible in accommodating foreign ions and elements than the crystalline phases. However, enough attention has not been given to investigate the origin, composition and role of glass in vitreous ceramics. Researchers working in other disciplines of materials have realised the important role of glass in consolidating, sintering and engineering of materials. For example, some of the important properties of glass include a) its fluidity that permeates the microstructure of the body resulting in densification without compromising the mechanical properties of the product, b) its viscosity to control crystal growth rate, and c) its fluxing behaviour to dissolve elements/compounds to enhance crystal nucleation rates or accommodate ions to enhance a desired property and suppress the undesired one. Low melting glasses are also being used as binders to consolidate alloy flakes at low temperatures that would otherwise require high uneconomical sintering temperatures or would cost transformation of the required phases or crystal size into undesired phases or crystal size 17. Furthermore, glass compositions are being tailored to suppress the crystallization of specific crystal phases and accelerate densification of the product via viscous flow prior to crystalization18-19. Similarly, to combat issues related to waste disposal and environment protection, ceramists are working to explore various ways to replace feldspar with waste or scrap alkali silicate glass. Initial results suggest that such replacements not only provide the relevant industry with a cheaper alternative for feldspar but also improve the quality of products. The observed lower sintering temperature (by \(~100^\circ\mathrm{C}\) than feldspar based porcelain makes it an economical alternative as well 20-23. Bragança et al 24 investigated the effect of the grain size of constituent quartz on the mechanical properties of triaxial porcelain. They attributed the toughness increase to the micro-crack toughening of the glass matrix coming from the stresses developed due to thermal expansion coefficient mismatch between the quartz particles and the glass matrix upon cooling. Similarly, most recently 25 it was reported in a study regarding the relationship between the microstructure and mechanical–technical properties of stoneware tile products that the stresses set up in the glass matrix, induced by the quartz grains attributed to the increase in toughness. This shows that an increase in the amount, size or interlocking of mullite 13 may improve the mechanical properties of porcelain bodies but the major contribution to strength comes from the stresses developed in the glassy matrix.

In order to explore various ways of utilizing the flexibility of glass, the role of glass in tailoring microstructures and properties of materials for specialized applications needs detailed investigations. Although triaxial porcelains are complex systems but they comprise of a high vol.% of glass. It is the purpose of this paper to present data on composition of some commercial porcelain and then discuss and review the origin, composition and role of glass in model and commercial tri-axial porcelain bodies.

EXPERIMENTAL
Commercial porcelain samples were collected from a number of manufacturers (Stoke-on-Trent, England). Model porcelain bodies were prepared as described elsewhere 16 using laboratory-scale mixing, ball milling and hand granulation. For X-ray Diffraction, raw powders of each and every body ingredient individually and as-mixed and milled powders of the model body were sieved through <325 mesh. For fired products, the surfaces were removed from the samples to exclude any surface effects and then ground in a mortar and pestle system to the required particle size. The powders were filled into the sample holders and scanned from 2θ=10°→60°, at a scanning speed of 0.5°/min, using a Philips diffractometer (with CuK\textalpha radiation, \(\lambda = 0.1541838 \text{ nm}\)) at 50 kV and 30 mA. The diffractometer was calibrated with an \(\alpha\)-quartz standard before use. JCPDS Cards 5-490 (\(\alpha\)-quartz), 15-776 (mullite), and 10-173 (corundum) were used to identify the observed crystal phases. For Scanning electron microscopy (SEM), specimens fired to temperatures above 1100°C were polished using 6, 3 and 1/4 \(\mu\)m diamond pastes after grinding with cerium oxide powders as abrasive and water as lubricant. The polished surfaces were etched for 3 min in 5% aqueous HF solution. The samples were then gold/carbon coated before examination in a Jeol 6400 SEM operating at 20 kV. Samples fired to low temperatures which could not be polished, were just smoothened and carbon coated before
microscopy. For transmission electron microscopy (TEM), 1 x 1.5 cm² pieces were cut from the bodies using fine cutting diamond saw and thinned to 100 µm with a diamond grinding wheel and Cerium Oxide powder and water. Circular discs (3 mm in diameter) were cut using ultrasonic drill and centres of the discs were dimpled to 25 µm with a dimpling machine. Argon ion thinning was used to fabricate electron transparent samples. Finally the samples were carbon-coated and examined in the Philips 420 and JEOL 3010 TEM.

RESULTS AND DISCUSSION

Figure 1 shows X-ray Diffraction (XRD) patterns from the constituent raw materials (quartz, feldspar and clay) used in the model porcelain body and as-mixed and milled porcelain body on top. XRD peaks due to crystal phases (present in the constituent raw materials) in the as-mixed and milled porcelain body can be accurately identified in this figure. The phase evolution upon firing can be systematically followed. Peaks labelled as Q are from α-quartz, K from kaolinite and F from feldspar which is a mixture of microcline and albite.

Figure 2 shows XRD pattern of as-mixed and milled porcelain body (bottom) and samples fired for 3 hours at 600ºC to 1500ºC (at 100ºC interval). The absence of XRD peaks due to kaolinite at 600ºC indicates the transformation of kaolinite into metakaolin at some temperature below 600ºC consistent with previous studies. Peaks due to feldspar are present up to 1000ºC but decrease in intensity with further increase in firing temperature showing its gradual melting until its complete dissolution at 1200ºC [Figure 2].

This indicates that melting of feldspar or in other words glass formation becomes detectable via XRD after firing at 1100ºC, despite the evidence that glass formation would begin at a temperature lower than 1000ºC. Similarly, the formation of mullite begins at ~1000ºC as revealed by TEM. However, small changes in smoothness of the XRD plot at 2θ=26.28º (the position of the most intense mullite peak) appeared at ~1200ºC. This was obviously due to small vol. % of mullite forming at lower temperatures (<1200ºC). Clearly distinguishable mullite XRD peaks are observed at temperature ≥1300ºC which increases in intensity with increase in firing temperature. The dissolution of quartz begins at about 1200ºC as revealed by SEM, however, due to small volume percentage of melted quartz; its dissolution is not visible on the XRD spectrum until the firing temperature increases beyond 1400ºC.

The appearance of a peak “C” at 21.96° corresponding to d-spacing 4.044Å, which is not visible on the spectra from samples fired to

![Figure 1](image-url)

**Figure 1:** X-ray Diffraction patterns from the raw materials (quartz, feldspar and clay) used in the model porcelain body with the spectrum from the unfired as-mixed and milled porcelain body on top. Peaks labelled as Q are from α-quartz, K from kaolinite and F from feldspar.
temperatures $\leq 1400^\circ$C, indicates the transformation of quartz into cristobalite. SEM of this sample revealed the presence of cracked quartz grains. As explained earlier, the quartz grains may crack due to the thermal expansion co-efficient mismatch between the crystalline quartz ($\alpha \approx 23 \times 10^{-6}$ K$^{-1}$) and the surrounding glass ($\alpha \approx 3 \times 10^{-6}$ K$^{-1}$); however, the XRD observation of cristobalite in the sample with cracked quartz grains suggests that the observed cracking may be due to the partial transformation of quartz into cristobalite. Thus the triaxial porcelain body fired at 1500$^\circ$C contains partially dissolved mullite, partially dissolved quartz (partially transformed into cristobalite) in a glassy matrix as indicated by the large amorphous hump on the XRD spectrum for sample fired at 1500$^\circ$C.

Figure 3 (a-b) illustrates that the microstructure of porcelain bodies fired to $\leq 900^\circ$C. This consists of sharp-edged $\alpha$-quartz grains (Q) of irregular shape, clay relict agglomerates (C) and feldspar grains in a fine grained mixture (MX) comprising feldspar, clay and quartz. Inspection of Figure 4a shows that at 1000$^\circ$C, all the micro-regions and grains observed at $\leq 900^\circ$C are still present. However; the appearance of a dark phase (L) at the clay relict agglomerate boundaries, obviously in contact with the fine grained feldspar and in the matrix, suggests the formation of liquid phase. The observation of the liquid phase in the samples fired to 1000$^\circ$C indicates that the formation of liquid has begun at some temperature lower than 1000$^\circ$C. The melting temperature of low melting flux is at least well above 1000$^\circ$C; therefore, the only explanation for liquid formation at $\sim 985^\circ$C (about 15$^\circ$C lower than 1000$^\circ$C) may be due to eutectic melting in the micro-regions of eutectic composition 9.5 K$_2$O-10.9 Al$_2$O$_3$-79.8 SiO$_2$. Schuller suggested that amorphous silica discarded during metakaolin formation may also assist eutectic melting at $\sim 900^\circ$C. However, in the present study, the only detectable liquid formation was observed in samples fired to 1000$^\circ$C.

As the melting process proceeds, the clay relict agglomerates containing feldspar relict grains become more resolvable and distinguishable from the pure clay relict agglomerates, particularly in back scattered SEM images (BSI). At 1100$^\circ$C, the amount of the dark liquid phase increases and the inhomogeneous distribution of pure clay and mixed clay plus feldspar relicts becomes clearly distinguishable (Figure 4b). The edges of the quartz grains (Q) are still sharp enough to confirm that the dissolution of quartz has not yet begun.

Figure 2: XRD pattern of as-mixed and milled porcelain body (bottom) and the XRD patterns from samples fired for 3 hours at 600$^\circ$C to 1500$^\circ$C (at 100$^\circ$C interval).
The greater amount of the dark liquid phase (L) in the feldspar relics containing regions than in the pure clay relics suggests the faster melting of feldspar grains than the other body ingredients. Thus up to 1100°C, only feldspar relics and clay relics mixed with or adjacent to fine grained feldspar relics contribute to the glassy phase. Figure 5a shows SEI of a hard commercial porcelain sample showing α-quartz grains (Q), clay relict agglomerates (C), mixed clay and feldspar relics (C+F) and a fine grained mixture (MX) comprising feldspar, clay and quartz.

Figure 3: Secondary electron SEM image (SEI) of an un-etched pressed porcelain body fired at a) 600°C and b) 900°C, showing α-quartz grains (Q), clay relict agglomerates (C), mixed clay and feldspar relics (C+F) and a fine grained mixture (MX) comprising feldspar, clay and quartz.
and grow into the feldspar relics, feldspar relics containing elongated secondary mullite (S) only and corundum grains (A). Note the presence of corundum grains inside clay and feldspar relics with no liquid phase surrounding them whereas the quartz grains appear as being isolated from the other constituent phases by the silica-rich solution rim. Considering the variation in size of mullite crystals in various micro-regions, it becomes evident that it is the composition and hence viscosity or fluidity of the surrounding glassy phase which suppresses or enhances the growth rate of the crystal phases. Secondly, the variation in the thermal expansion co-efficient of

![Back scattered SEM image (BSI) of an etched model porcelain fired at a) 1000°C and b) 1100°C, showing quartz grains (Q), clay relict agglomerates (C), clay relict agglomerates containing feldspar (C+F) and feldspar grains (F) in a fine grained mixture (MX) comprising feldspar, clay and quartz. The dark phase (L) at the clay relict agglomerate boundaries and in the matrix suggests liquid formation. Note the increase in dark liquid phase (L) with temperature permeating the microstructure in Figure 4b. After Iqbal & Lee (2008) with permission from Blackwell Publishing Ltd.]

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the crystal phases and the surrounding glassy phase(s) determine the level of micro-stresses produced which influence the mechanical properties of the product. As mentioned earlier, the densification temperature of the body is also dependent upon the temperature at which enough liquid forms to fill the pores and voids. Figure 5b is a bright field TEM image of an area observed in hard commercial porcelain sample showing the variation in glass composition between an α-quartz grain and a clay relict micro-region (primary mullite crystals in glass). EDS from the α-quartz grain and three spots labelled as 1, 2, and 3 detected 100 wt% Si whereas spots 4 contained 19.9 wt% Al₂O₃ and 80.1 wt% SiO₂ (i.e., 12.8 mol% Al₂O₃ and 87.2 mol% SiO₂) and spot 5 contained 39.9 wt% Al₂O₃ and 61 wt% SiO₂ (i.e., 42.9 mol% Al₂O₃ and 57.1 mol% SiO₂). No alkali content was detected in this region. The compositions determined for spots “4” and “5” with no alkali content and enough alumina suggest the possibility of contribution from nano-scale primary mullite crystals to the observed EDS spectra and the composition of the glass is probably close to pure SiO₂. Furthermore, the cooling rates of porcelain bodies are commonly too slow to suppress crystallization and aluminosilicate glasses are prone to crystallization of mullite. Therefore, in the micro-regions with no feldspar, the only crystalline phases observed were quartz and mullite, and the composition of the glass was close to pure SiO₂. On the one hand, it is difficult to isolate the crystals from the surrounding glassy matrix and on the other hand, the EDS spectra from the glassy phase are overlapped by contributions from the nano-scale crystalline phases and therefore, the results regarding compositional analyses from such complex systems may not be very accurate. In general, the observed composition of the glassy phase in porcelain bodies was heterogeneous e.g. in clay relics where nano-scale primary mullite crystals are embedded in the glass, the K₂O-content varied from 0-9 wt%. The wt% composition (according to supplier’s data sheet) of the English China Clay used in this study was 48 SiO₂, 37 Al₂O₃, 0.77 Fe₂O₃, 0.07 CaO, 2.3 Na₂O, 0.3 K₂O, 0.3 MgO and 0.03 wt% TiO₂. Therefore, the lower limit of K₂O (≤ 0.3 wt%) observed in the glassy phase in clay relict can be justified but higher amounts of K₂O suggest uneven mixing of the body ingredients. In feldspar relics i.e. from among the elongated secondary mullite crystals, the K₂O content varied from 0-13 wt% where as the supplier’s reported composition of the feldspar (Nepheline Syenite) contained 8.9 wt% K₂O. This is again an evidence of inhomogeneous mixing. Similarly, the Al₂O₃ and SiO₂ contents varied in such a manner that no range could be given to describe the observed heterogeneity. The obvious reasons for the variation of silica and alumina contents were the regions with 100 wt% of silica in the matrix and overlapping of the EDS spectra from glass by the contribution from nano-scale primary mullite crystals in the alumina-rich regions. In fact, in tri-axial porcelains, the transformation of phases occur in such a manner that keeps these systems far from equilibrium e.g. at temperatures lower than 1000ºC, the initial body ingredients are present as distinct and distinguishable micro-regions and at higher temperatures (from 1000ºC to 1300ºC) the dissolution of quartz, and mullite formation and growth occur simultaneously that continuously changes the composition of the glass. At temperatures above 1400ºC, the simultaneous partial dissolution of mullite and quartz keeps the system far from equilibrium. Previous studies regarding the composition analyses of the constituent glass phase in porcelain bodies are also incongruous. Hermansson and Carlsson examined the glassy phase in 30 whiteware bodies and reported that the wt% composition of glass phase was homogenous (76 SiO₂, 16 Al₂O₃, 7 K₂O, 1 CaO) while Klykova et al. reported that the Al₂O₃:SiO₂ of the glassy phase varied. Furthermore, the raw materials commonly used in porcelain manufacturing are not highly pure and therefore, compositional variations are not unexpected. The observed variation in mullite crystal size as seen in Figure 5a, the mullite crystal size is the smallest in pure clay relics due to the highly viscous silica glass matrix with with no or minimum alkali content. At the clay-matrix or clay-feldspar interface, the mullite crystal size is larger than those observed in the pure clay relics but smaller compared to those in the centre of the matrix or pure feldspar relics (Figure 5a).

This is consistent with the variation in the alkali content of the constituent raw materials and hence viscosity of the surrounding glassy phase. The size of the primary mullite crystals in the vicinity of the partially dissolved quartz in Figure 5b and the size of the secondary mullite in the vicinity of the feldspar relics in Figure 5a is worth-seeing. Thus, it is the viscosity or fluidity

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Figure 5: a) SEI of a hard commercial porcelain sample showing $\alpha$-quartz grains (Q) surrounded by silica-rich solution rims (R), regions of clay relics containing primary mullite (P), interfaces between clay and feldspar relics (I) from where secondary mullite (S) originate and grow into the feldspar relics, feldspar relics containing elongated secondary mullite (S) only and corundum grains (A). Note the presence of corundum grains inside clay and feldspar relics with no liquid phase surrounding them whereas the quartz grains appear as being isolated from the other constituent phases by the silica-rich solution rim. b) Bright field TEM image of an area observed in hard commercial porcelain sample showing the variation in glass composition between an $\alpha$-quartz grain and a clay relict micro-region (primary mullite crystals in glass). After Iqbal & Lee, 15 Courtesy Blackwell Pub. Co. Ltd.

of the glassy phase that suppresses or enhances the crystal growth. A third form of mullite “tertiary mullite” also forms in hard commercial porcelains containing corundum grains 15. The formation of tertiary mullite again comes from the alumina rich liquid surrounding...
the partially dissolved corundum grains. Thus the size, shape and composition \(^{15}\) of mullite crystals depend to a greater extent upon the composition of the relevant raw material relict and viscosity of the glass. Therefore, a need was felt to form an alternative notation for the types of mullite formed in porcelains. Consequently, Iqbal and Lee \(^{16}\) suggested Type I for cuboidal low aspect ratio (1–3:1) primary mullite derived from pure clay, Type II for 3–10:1 aspect ratio secondary mullite detected in feldspar-penetrated clay relicts and Type III for very high aspect ratio (30–40:1) secondary mullite needles originating at clay-feldspar-relicts interfaces and growing into the highly fluid feldspar relicts obviously 10-30:1 comes in type-III. Fluidity can increase with increase in firing temperature or through the composition of the flux. For example, the viscosity of melts derived from Na\(_2\)O-containing fluxes is less than those derived from K\(_2\)O-containing fluxes. Therefore, the crystal growth rates will be higher in the latter than the former fluxes. Furthermore, the observation of a variety of mullite in different micro-regions of the same sample (fired at a commercially applied temperature) favours the influence of composition and hence viscosity of the glass matrix rather than the firing temperature.

**CONCLUSIONS**

The variation in the composition, shape and size of various types of mullite observed in porcelain bodies depends on the composition and hence viscosity of the surrounding glass-matrix in porcelain bodies. It is difficult to measure the exact composition of the glass phase, particularly in the clay relicts and clay plus feldspar relicts as the crystals embedded in the glass also contribute to the EDS spectra from the glass. The composition of glass close to quartz grains and clay relicts is highly silica-rich. The varying alkali content (0 to 9 wt%) in clay relicts and 0 to 13wt% in feldspar relicts may demonstrate the uneven distribution of the constituent phases or incomplete mixing of the body ingredients.

**REFERENCES**


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